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The Determination of Atomic Mass Doublets by Means of a Mass Spectrometer*

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A double-focusing mass spectrometer employing a 90° electrostatic analyzer followed by a 60° magnetic analyzer has been constructed having a resolution sufficiently great to permit mass difference measurements by the familiar doublet method. High stability is obtained by use of an auxiliary mass spectrometer tube which compensates for fluctuations in both the magnetic field and the source of potential for the deflecting and accelerating plates of the main spectrometer. Ion currents are measured electrically and data recorded automatically.

The doublets determined and their values in 10^{-4} amu are as follows: $D_2O^{16}-A^{40}/2$, 419.67 ± 0.18; $D_2O^{16}-Ne^{20}$, 307.21 ± 0.39; $Ne^{20}-A^{40}/2$, 112.80 ± 0.18; $(C^{12})_2H_4-C^{12}O^{16}$, 364.43 ± 0.22; $(N^{14})_2-C^{12}O^{16}$, 112.80 ± 0.13; $(C^{12})_3H_8-(N^{14})_2O^{16}$, 617.6 ± 0.9; $C^{12}H_4-O^{16}$, 364.78 ± 0.22; $C^{12}H_2-N^{14}$, 125.86 ± 0.13; $(C^{12})_3H_4-A^{40}$, 688.77 ± 0.35; $(C^{12})_3H_4-Ca^{40}$, 685.39 ± 0.46; $Ca^{40}-A^{40}$, 3.2 ± 0.8; D_2-He^4, 256.12 ± 0.09; $H_2O^{16}-A^{36}/2$, 267.02 ± 0.40.

I. INTRODUCTION

THE generally accepted direct method of measuring atomic masses has been to use a double-focusing mass spectrograph.[1] Ney and Mann[2] have shown that, with a single-focusing mass spectrometer of the type now commonly used for measuring isotope abundances, remarkably accurate mass measurements are possible if one is content to work with molecular ions. Measurements on molecular ion fragments are not possible, since these fragments usually acquire initial kinetic energies in the dissociation process in which they are formed. They will then be focused in the instrument at lower energies than are the molecular ions, and a measurement of their relative positions in the mass spectrum will not be an accurate measure of the mass of the fragment. This limitation can be overcome only by using a double-focusing instrument, that is, one in which all ions of the same mass leaving an ion source and having a range of energies as well as a range of angles will be refocused at the same point.

A double-focusing mass spectrometer employing features of the usual single-focusing mass spectrometers has certain advantages over a conventional mass spectrograph. (1) The general procedure in making measurements differs sufficiently from that employed with mass spectrographs, so that the same systematic errors are not likely to appear in the two methods. (2) The mass doublet to be studied can be investigated carefully before actual measurements are taken. The intensities of the two peaks can be adjusted to be equal and measurement of resolution and other factors which might affect the mass measurement can be made. (3) Since focusing need be achieved at only one point, some of the compromises necessary in the design of the usual photographic plate instrument need not be made. (4) The ion currents are steady and hence may be measured conveniently with electrical instruments.

Among the disadvantages are: (1) some valuable mass doublets are not obtained, e.g., $D_3{}^{+}-(C^{12})^{++}$; (2) the photographic method, giving current integration, permits measurement of extremely small or unsteady ion currents; and (3) the doublet is scanned by changing the difference in potential across an electrostatic ana-

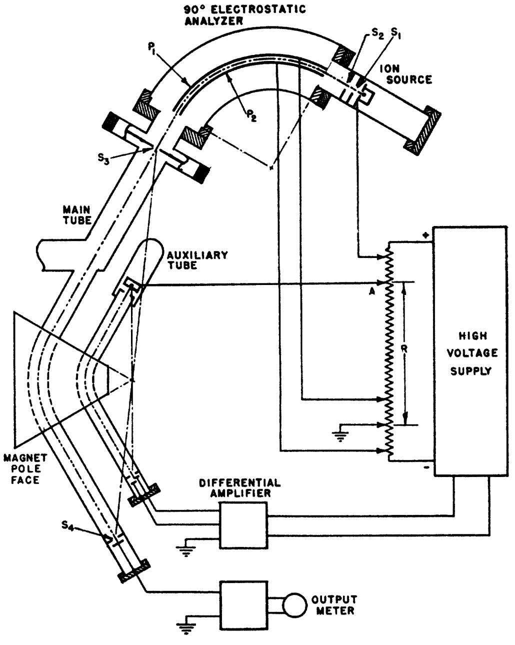

FIG. 1. Schematic drawing of mass spectrometer tubes showing action of regulation circuit. Mean radius of cylindrical electrostatic analyzer 18.87 cm. Separation of plates P_1 and P_2, 1 cm. Radius of magnetic analyzer in main and auxiliary tubes, 15.24 and 7.62 cm, respectively. Distances of S_3 and S_4 from effective pole faces are 34.77 and 20.73 cm, respectively. Asymmetrical construction reduces width of beam at S_4 owing to divergence of ion beam. S_1, S_2, S_3, and S_4 are 0.0025, 0.033, 0.25, 0.0025 cm, respectively, for most of data reported here. S_1 and S_2 are separated by 3.71 cm. Main and auxiliary tube ion accelerating potentials are approximately 4000 and 1000 v, respectively. Hence, gas used in auxiliary tube has approximately the same molecular weight as the doublet to be studied.

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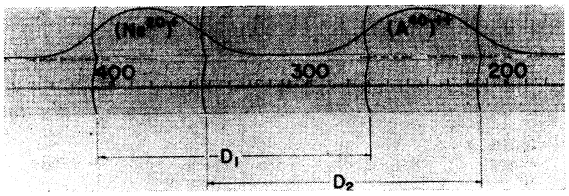
[1] For the different types of instruments used see F. W. Aston, *Mass Spectra and Isotopes* (Longmans, Green and Co., New York, 1942), second edition.

[2] E. P. Ney and A. K. Mann, Phys. Rev. **69**, 239 (1946).



$$\frac{\text{Mass difference}}{\text{Mass number}}=\frac{1}{1776}$$

FIG. 2. Mass doublet $(Ne^{20})^+-(A^{40})^{++}$. Mass difference is found by measuring distances on charts between corresponding half-heights of peaks. Distances are converted to mass units.

lyzer (and also changing the accelerating potential applied to the ions). Stray electric fields caused by charges on the analyzer plates could lead to errors. However, in practice this effect was shown to be negligible by comparing the mass difference of adjacent hydrocarbon ion peaks with the known mass of the hydrogen atom.

II. THE APPARATUS

Figure 1 shows a schematic view of the essential parts of the apparatus used in the present investigation.[3] Ions produced by electron impact or thermionic emission in the source of the main tube are sent through the collimating slits S_1 and S_2 into a 90° electrostatic analyzer. An energy spectrum is produced in the focal plane containing the slit S_3. Refocusing occurs at S_4 after the ions have passed through the asymmetrical 60° magnetic analyzer. The ion currents are measured with a vibrating reed electrometer and recorded by one of the channels of a Brush two-channel magnetic oscillograph.

In order to minimize the effect of fluctuations in the magnetic field or ion deflecting voltage, a second and smaller auxiliary mass spectrometer tube is mounted in the same magnetic field as is employed for the larger one. This tube is very similar in construction to those ordinarily used for isotope abundance measurements.[4] It differs, however, in that a double collector system is used which is coupled to a differential amplifier. This tube is so adjusted that the ion current is split, with one-half going to each collector plate. Under these conditions there will be no output from the differential amplifier. If now the magnetic field or accelerating voltage applied to the ions should change, the ion beam will shift and a signal will appear at the output of the differential amplifier. This signal is fed into the high voltage supply in a sense which tends to restore the ion beam to its original position. Since both spectrometer tubes obtain their ion accelerating and deflecting potentials from a common voltage divider, the action of the small tube corrects for fluctuations which would normally disturb the paths of ions in the main tube.

A mass spectrum in the main tube is obtained by varying resistance R, i.e., by moving the position of tap A. Since the auxiliary tube and the associated high voltage supply and divider constitute an inverse feedback loop, it may be shown readily that the change in mass of the ions collected in the main tube is related to the change ΔR in R by the relation,

$$\Delta m/m=(\Delta R/R)[G/(G+1)],$$

where G is the open circuit gain of the feed-back loop.

III. RESULTS

Figure 2 shows a typical chart obtained for the doublet $(Ne^{20})^+-(A^{40})^{++}$ when a mixture of neon and argon was placed in the main tube. Attached to the shaft of the 10-turn, 1000-ohm helical potentiometer used for scanning the mass spectrum is a 100-tooth gear on which ride Microswitches which open and close as the teeth go by. Signals from circuits attached to the switches are impressed on the second channel of the oscillograph and are printed simultaneously as indicated. Small lines indicate 1-ohm steps, large ones 10-ohm steps. Three large lines together indicate full turns (100 ohms) of the helical potentiometer. Since R is approximately 250,000 ohms, each small division represents a change of mass of 1/250,000. Inasmuch as the resistance R is in effect recorded simultaneously with the mass spectrum, errors associated with the running of the recorder are eliminated. The helical potentiometer is carefully calibrated along its entire length.

A run consisted of 10 consecutive spectra such as shown in Fig. 2, the potentiometer being driven alternately clockwise and counterclockwise. Distances D_1 and D_2 were projected on the reference scale as shown. From the calibration of the potentiometer the corresponding values ΔR_1 and ΔR_2 are determined. The average of the 20 resistance differences is then taken as ΔR for the run. G was determined before and after

TABLE I. Doublets at mass 20.

Row	Doublet	No. of runs	Av. in 10^{-4} amu	Previous work
1	$D_2O^{16}-A^{40}/2$	5	419.67 ± 0.18 (0.08)	$418.9\ \pm2.0$[a]
2	$D_2O^{16}-Ne^{20}$	4	307.21 ± 0.39	$306.5\ \pm1.0$[a] $308.3\ \pm4.0$[b]
3	Row 1 − row 2		112.46 ± 0.43	
4	$Ne^{20}-A^{40}/2$	2	112.65 ± 0.40	$113.0\ \pm2.0$[a] $108.8\ \pm3.0$[b] 111.42 ± 0.38[c]
5	$(D_2O^{16}-A^{40}/2)-(D_2O^{16}-Ne^{20})$	2	112.84 ± 0.21	

[a] E. B. Jordan and K. T. Bainbridge, Phys. Rev. **51**, 385 (1937).
[b] F. W. Aston, Proc. Roy. Soc. (London) **A163**, 391 (1937).
[c] J. Mattauch, Physik. Z. **39**, 892 (1938).

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[3] A preliminary report on the apparatus and some results presented here have already been given: Nier, Roberts, and Franklin, Phys. Rev. **75**, 346 (1949); T. R. Roberts and A. O. Nier, Phys. Rev. **77**, 746 (1950).

[4] A. O. Nier, Rev. Sci. Instr. **18**, 397 (1947).

TABLE II. Doublets containing combinations of C^{12}, H, N^{14}, and O^{16}.

Row	Doublet	No. of runs	Av. in 10^{-4} amu	Previous work
1	$(C^{12})_2H_4-C^{12}O^{16}$	3	364.43±0.22 (0.19)	
2	$(C^{12})_2H_4-(N^{14})_2$	12	251.70±0.25 (0.07)	
3	Row 1−row 2		112.73±0.33	
4	$(N^{14})_2-C^{12}O^{16}$	2	112.73±0.14	111.7 ±2.0[a] 112.22±0.40[b]
5	$[(C^{12})_2H_4-C^{12}O^{16}]-$ $[(C^{12})_2H_4-(N^{14})_2]$	2	113.26±0.37	
6	$(C^{12})_3H_8-C^{12}(O^{16})_2$	8	729.68±0.44 (0.18)	
7	$(C^{12})_3H_8-(N^{14})_2O^{16}$	4	617.6 ±0.9	
8	Row 6−row 7		112.1 ±1.0	
9	$C^{12}H_4-O^{16}$ (Compare with row 1 and ½ row 6)	2	364.80±0.63	364.9 ±0.8[a] 360.1 ±1.6[c] 363.81±0.28[d] 364.2 ±0.9[e] 363.2 ±0.35[f]
10	$C^{12}H_2-N^{14}$ (Compare with ½ row 2)	6	125.97±0.21	127.4 ±0.8[a] 124.5 ±0.7[c] 125.78±0.21[d] 125.7 ±0.6[e] 125.60±0.15[f] 125.22±0.12[g]

[a] K. T. Bainbridge and E. B. Jordan. Data in article by M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. **9**, 370 (1937).
[b] J. Mattauch, Physik. Z. **39**, 892 (1938).
[c] F. W. Aston, Proc. Roy. Soc. (London) **A163**, 391 (1937).
[d] J. Mattauch and A. Flammersfeld, *Isotopenbericht* (Verlag. Z. Natur., Tübingen, 1949).
[e] Asada, Okuda, Ogata, and Yoshimoto, Proc. Phys. Math. Soc. Japan **22**, 41 (1940).
[f] E. B. Jordan, Phys. Rev. **60**, 710 (1941).
[g] H. Ewald, Z. Naturforsch. **1**, 131 (1946).

each run. Its value lay between 60 and 100 for the data presented here and did not vary more than a few percent during a run.

IV. MASS 20 DOUBLETS

Table I gives the results for several doublets measured at the mass 20 position. Since readings taken at one time were very consistent, usually not more than one run on a given doublet was taken on a single day. The runs used in computing the averages in this and other tables of this paper were taken over a period of several months; the spectrometer ion source and electronic components frequently underwent revision between runs.

TABLE III. Doublets at mass 40.

Row	Doublet	No. of runs	Av. in 10^{-4} amu	Previous work
1	$(C^{12})_3H_4-A^{40}$	8	688.77±0.35	679 ±6[a] 679.3±0.7[b] 693.0±2.3[b]
2	$(C^{12})_3H_4-Ca^{40}$	5	685.39±0.46	
3	Row 1−row 2		3.38±0.58	
4	$Ca^{40}-A^{40}$	Too small for direct measurement		
5	$[(C^{12})_3H_4-A^{40}]-$ $[(C^{12})_3H_4-Ca^{40}]$	5	3.2 ±0.8	

[a] F. W. Aston, Proc. Roy. Soc. (London) **A163**, 391 (1937).
[b] Okuda, Ogata, Aoki, and Sugawara, Phys. Rev. **58**, 578 (1940).

The probable errors given were computed by assuming the individual runs as independent when four or more runs were taken. The charts were read to the closest tenth of an ohm. Because of the finite size of wire on the helical potentiometer, a single reading could be determined only to 0.2 ohm. In many instances the agreement between runs was so good that the probable error was extremely small. In such cases the probable error given was taken arbitrarily as one-half the smallest difference which could be determined on the potentiometer due to the finite wire size. Where this was done, the actual computed probable error is given in parentheses under the assumed value.

Row 5 differs from row 3 in that the runs were taken in immediately consecutive pairs to determine the $Ne^{20}-A^{40}/2$ difference more accurately. Our final value for this difference is 112.80±0.18, a weighted average of rows 4 and 5. This result agrees best with that of Bainbridge and Jordan. The excellent agreement between rows 4 and 5 show that comparison with a third ion gives a reliable doublet measurement. This method can be employed for doublet separations which are too small to measure directly. As shown in Fig. 2, the lower limit of complete resolution at present is about 1 in 2000.

V. DOUBLETS CONTAINING C^{12}, H, N^{14} AND O^{16}

Table II gives the results for various doublets containing combinations of C^{12}, H, N^{14}, and O^{16}. The ions used in the present work were molecular ions except O^{16} from carbon dioxide, N^{14} from nitrogen gas, and $C^{12}H_2$ from methane or ethylene. The first five rows in Table II correspond with those in Table I and, as before, the best value for $(N^{14})_2-C^{12}O^{16}$ is obtained from rows 4 and 5 as 112.80±0.13. Still another determination of this doublet is given in row 8 but was not included because with its higher probable error it would have little influence on the final value.

As shown in row 9, row 1 and one-half the value in row 6 also give the fundamental doublet, $C^{12}H_4-O^{16}$, which has been measured extensively by previous workers. If the probable error of ±0.18 derived directly from the data is used for row 6, the weighted average

TABLE IV. D_2-He^4 and $H_2O^{16}-A^{36}/2$ doublets.

Doublet	No. of runs	Av. in 10^{-4} amu	Previous work
D_2-He^4	2	256.12±0.09	256.1 ±0.4[a] 255.1 ±0.8[b] 256.04±0.08[c]
$H_2O^{16}-A^{36}/2$	5	267.02±0.40	271 ±3.6[b]

[a] K. T. Bainbridge and E. B. Jordan, Phys. Rev. **51**, 384 (1937).
[b] F. W. Aston, Proc. Roy. Soc. (London) **A163**, 391 (1937).
[c] H. Ewald, Z. Naturforsch. **5a**, 1 (1950).

of our three determinations is 364.78±0.22 (0.08). This measurement agrees best with that of Bainbridge and Jordan.

Combining our results in rows 2 and 10 we obtain a $C^{12}H_2-N^{14}$ value of 125.86±0.13 (0.04). This result is in substantial agreement with three of the four most recently published measurements.

VI. OTHER DOUBLETS

A preliminary report of the data in Table III has already been given.[5] In this case the $Ca^{40}-A^{40}$ separation was too small to measure directly so that the result given in row 5 is our best value.

Calcium ions were obtained by heating the metal in a furnace in the ion source. The $(C^{12})_3H_4$ ions were fragment ions obtained from cyclopropane. A correction amounting to 0.4 percent of the doublet width in rows 1 and 2 was made for the unresolved $(C^{12})_2C^{13}H_3$ peak on the low mass side of the $(C^{12})_3H_4$ peak. A correction of the same general type was made for C^{13} containing hydrocarbon ions in Table II. Failure to make such a correction probably accounts for the discrepancies in Okuda's two measurements listed in row 1. The abnormally high relative intensity of C_3H_3 ion fragments from hydrocarbons make this correction especially important for $(C^{12})_3H_4$ peaks. This isotopic correction has no effect on the result given in row 5.

Two other recent doublet measurements are listed in Table IV.

The above results indicate the practicability of using the mass spectrometer for precise mass difference measurements. A subsequent paper will discuss the determination of the isotopic weights of secondary mass standards.

The authors wish to acknowledge the very able assistance of R. B. Thorness and E. G. Franklin in designing and constructing the instrument, and the aid of W. H. Johnson and H. A. Lindgren in recording and computing the data. The construction of the apparatus was aided materially by grants from the Graduate School and the Minnesota Technical Research Fund subscribed to by General Mills, Inc., *Minneapolis Star and Tribune*, Minnesota Mining and Manufacturing Company, Northern States Power Company, and Minneapolis Honeywell Regulator Company.

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[5] T. R. Roberts and A. O. Nier, Phys. Rev. 79, 198 (1950).

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Polonium Isotopes Produced with High Energy Particles*

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We have investigated four new isotopes of polonium produced from bismuth and lead by high energy spallation and have studied their decay products, which include three new lead and bismuth activities. The mass assignments are made by the identification of known activities as decay products. Some of the properties of these new isotopes are as follows:

Isotope	Half-life	Mode of decay	Energy in Mev	
			Alpha-particles	Gamma-rays
Po^{205}	1.5 hr	*EC*, α	5.22±0.10	
Po^{204}	3.8 hr	*EC*, α	5.37±0.02	
Po^{203}	47 min	*EC*		
Po^{202}	52 min	*EC*, α	5.59±0.03	
Bi^{205}	14.5 days	*EC*		0.431, 0.527 0.550, 0.746 1.84
Bi^{202}	95 min	*EC*		
Pb^{198}	25 min	*EC*		

I. INTRODUCTION

POLONIUM has eight isotopes, beta-stable or with neutron excess, which occur in the natural radioactive series or the artificial neptunium series. Cyclotron-induced transmutations now make possible the production of neutron-deficient polonium isotopes. Templeton, Howland, and Perlman[1] have produced by this means the three isotopes Po^{206}, Po^{207}, and Po^{208}, and Kelly and Segrè[2] have found Po^{209}. The present work was undertaken to extend our knowledge of polonium to the even lighter isotopes which can be made by the 184-inch Berkeley cyclotron. We have observed the radioactivities of the next four isotopes, Po^{205}, Po^{204}, Po^{203}, and Po^{202}. Experiments designed to establish the decay products and mass assignments of these radioactivities led to the discovery of two radioactive species of bismuth and one of lead. Our work was greatly aided by a parallel investigation of bismuth and lead isotopes carried out in this same laboratory by Neumann and Perlman, who have already reported their results.[3]

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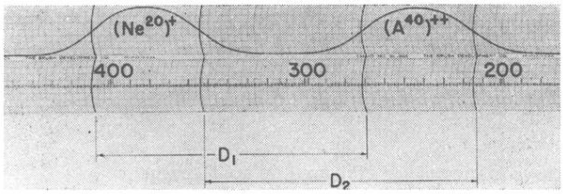
* This work was done under the auspices of the U. S. AEC.

[1] Templeton, Howland, and Perlman, Phys. Rev. 72, 758 (1947).

[2] E. L. Kelly and E. Segrè, Phys. Rev. 75, 999 (1949).

[3] H. M. Neumann and I. Perlman, Phys. Rev. 78, 191 (1950).



$$\frac{\text{Mass difference}}{\text{Mass number}}=\frac{1}{1776}$$

FIG. 2. Mass doublet $(\mathrm{Ne}^{20})^{+}-(\mathrm{A}^{40})^{++}$. Mass difference is found by measuring distances on charts between corresponding half-heights of peaks. Distances are converted to mass units.