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Atomic Masses of Mass-substandards H, D, ^{35}Cl and ^{37}Cl and of ^{14}N , ^{16}O

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In order to determine the atomic masses of the mass-substandards, H, D, ^{35}Cl and ^{37}Cl , the ten kinds of doublets involving these nuclides were measured by the digital peak matching method with the half height resolution of 300,000~500,000. These doublet mass differences were as follows: $(\text{C}_2\text{D}_6-\text{C}_3)=84,611.600 \pm 0.340$, $(\text{C}_2\text{D}_6-\text{H}^{35}\text{Cl})=107,934.900 \pm 0.540$, $(\text{C}_3-\text{H}^{35}\text{Cl})=23,321.830 \pm 0.630$, $(\text{C}_2\text{D}_6-\text{C}_3)=84,611.730 \pm 0.411$, $(\text{C}_3-\text{H}^{35}\text{Cl})=23,322.328 \pm 0.325$, $(\text{C}_2\text{D}_6-\text{H}^{35}\text{Cl})=107,933.422 \pm 0.538$, $(\text{C}_3\text{H}_2-\text{H}^{37}\text{Cl})=41,922.176 \pm 0.305$, $(\text{D}^{35}\text{Cl}-^{37}\text{Cl})=17,051.816 \pm 0.185$, $(\text{C}_2\text{D}_2-\text{C}_2\text{H}_4)=3,096.444 \pm 0.127$ and $(\text{C}_3\text{H}_8-\text{C}_3\text{D}_4)=6,192 \pm 0.265 \mu\text{u}$.

Using above doublet mass difference values as input data, the mass-substandards were calculated by least squares treatments. The results were $\text{H}=7,825.065 \pm 0.030$, $\text{D}=14,101.930 \pm 0.040$, $^{35}\text{Cl}=-31,147.21 \pm 0.20$ and $^{37}\text{Cl}=-34,097.10 \pm 0.22 \mu\text{u}$. Using these results and the previously measured doublets $(\text{C}_2\text{H}_4-^{14}\text{N}_2)=25,152.44 \pm 0.19$ and $(\text{C}_2\text{H}_4-\text{C}^{16}\text{O})=36,384.01 \pm 0.24 \mu\text{u}$, mass excess of $^{16}\text{O}=-5,085.75 \pm 0.25$ and $^{14}\text{N}=3,073.91 \pm 0.14 \mu\text{u}$ was obtained.

1. Introduction

During the last decade, the accuracy of atomic mass measurements has increased rapidly and that recently reported has attained in the order of magnitude of $10^{-8} \sim 10^{-9}$. However, the agreement between these mass values seems to be not so good with each other, even among the mass-substandards H, D, ^{35}Cl and ^{37}Cl . The causes of such disagreement may be due to the systematic errors included in each measurement. Under such present status in precise atomic mass measurements, the first thing to do must be the careful investigations on the systematic errors which

might be included in doublet mass difference measurements. And then, in order to determine the masses of mass-substandards within the accuracy of 10^{-8} or somewhat less, it may be worthwhile to calculate these masses combining the different kinds of doublets, in which they are involved, as many as possible.

From this viewpoint, the author previously investigated the systematic errors in the peak matching procedures and it was confirmed that the systematic errors can be almost eliminated.¹⁾ The mass differences of $(\text{C}_2\text{H}_4-\text{C}^{16}\text{O})$, $(\text{C}_2\text{H}_4-^{14}\text{N}_2)$, $(^{14}\text{N}_2-\text{C}^{16}\text{O})$ and $(\text{C}_2\text{H}_4-\text{C}_2\text{D}_2)$ were

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measured and the results obtained were reported elsewhere.¹⁾ In that case, the orthodox visual peak matching method was adopted and the closure error of the triplet ($\text{C}_2\text{H}_4-^{14}\text{N}_2-\text{C}^{16}\text{O}$) was estimated to be $0.26 \mu\text{u}$.

In the present work, for increasing the measurement accuracy of doublet mass differences, the visual peak matching method was replaced by the digital one using 400 channel pulse height analyzer. It is generally spoken that in the digital peak matching method, the mismatching degree of the order of $1/100 \sim 1/1000$ of a peak width can be recognized and the measuring accuracy obtained is improved by the factor $5 \sim 10$ than that in the visual one.

As a possible cause of systematic errors which had previously not considered, the effect of peak shapes on measured mass differences was also investigated. The six different treatments described below were adopted for checking above point, and the systematic difference depending on the peak shape could not be found out. Then the mass differences ($\text{H}^{35}\text{Cl}-\text{C}_3$), ($\text{H}^{35}\text{Cl}-\text{C}_2\text{D}_6$) and ($\text{C}_3-\text{C}_2\text{D}_6$) were measured, and from these doublet mass differences the preliminary atomic masses of D and ^{35}Cl were determined. Combining previously measured mass differences at mass 28, the atomic masses of H, ^{14}N and ^{16}O were determined. But, unfortunately, the closure error of the triplet ($\text{H}^{35}\text{Cl}-\text{C}_3-\text{C}_2\text{D}_6$) was over the error estimated from the errors attached to each doublet.

After these measurements, seven doublet mass differences involving C, D, H, ^{35}Cl and ^{37}Cl were measured and the masses of mass-substandards H, D, ^{35}Cl and ^{37}Cl were calculated by least squares treatments.

2. Experiments

The details of the characteristics of a mass spectroscopy used, the operating conditions and the peak matching procedures were previously reported elsewhere.¹⁻³⁾ So, here the author would like to begin to estimate the approximate amount of focus-defect of the machine, which might bring some systematic errors into the measured doublet mass differences.

2.1 Focusing Characteristics and Peak Shapes

The schematic view of the instrument is shown in Fig. 1. The parameters of the instrument are as follows:

$$a_e = 1093 \text{ mm}, a_m = 1200 \text{ mm}, \Phi_e = 84^\circ 50', \\ \Phi_m = 60^\circ, l_e' = 1340 \text{ mm}, l_m' = 1200 \text{ mm}, \\ l_e'' = 0.0 \text{ mm}, \text{ and } l_m'' = 4480 \text{ mm}.$$

With this arrangement of the fields, for the image magnification G and mass dispersion coefficient D the values of 1.37 and 22.4 mm (for 1 % mass difference), respectively, are obtained. And the resolving power at the focus point can be expected as follows.

$$\frac{D}{y''} = \frac{D}{G \cdot S} = 1.6 \times 10^3 \cdot \frac{1}{S} (S: \text{object slit width})$$

This asymmetric arrangement of the radial electrostatic and uniform magnetic fields gives the improvement by the factor of 1.5 in the resolving power than that expected from the symmetric ones.

In the case of electric detection of ions, which is used usually in the peak matching method, the half height resolution is equal to that of the photographic one when the collector slit of which width is equal to the image width is used. In the case of photographic detection, the photographic plate is set to have an angle of about 19° to the direction of the optical axis through

Fig. 1. Schematic view of the instrument.

the double focus point, because the focus planes of direction and energy have angles of 17° and 21° , respectively. And so, the dispersion and image width on the photographic plate are to be by 3.1 times greater than those in the direction perpendicular to the optical axis, and the mass dispersion D' and the image width y'' are 76 mm and $4.6 \cdot S$, respectively.

In the case of the digital peak matching method, the mismatching degree of the order of $1/100$ or less of a peak width can be recognized. So, if the peak shapes of doublet components are different in the order of such magnitude with each other, some systematic errors would be introduced in the measured mass differences.

When the ion beams of doublet components to be compared have different distributions in direction and/or energy with each other, their peak shapes at the

double focus point are different according to the second order aberration. So, it is necessary to estimate the image width caused by the second order aberration.

The image width y'' at the double focus point can be calculated as follows:

$$y'' = G \cdot S + D\gamma + D_{11}\alpha'^2 + D_{12}\alpha'\beta' + D_{22}\beta'^2,$$

where S is the object slit width, and D_{11} , D_{12} and D_{22} are the second order coefficients which have the values of $D_{11} = 5.4 \times 10^3$ mm, $D_{12} = -15.7 \times 10^3$ mm and $D_{22} = 3.5 \times 10^3$ mm.

When the object slit of 2μ is used, the image width is 2.7μ in the first order approximation and the resolving power is calculated to be 7.5×10^5 . When the α slit, direction limiting slit, placed at the entrance of the electric field and the β slit, energy limiting slit, placed at the exit of

the electric field of both 0.1 mm are used, $\alpha_{\max}$ and $\beta_{\max}$ are estimated to be 4×10^{-5} and 3.3×10^{-5} , respectively. Then, the image defects δy_{11} caused by D_{11} , δy_{12} (by D_{12}) and δy_{22} (by D_{22}) are obtained to be

$$\delta y_{11} = 5.4 \times 10^3 \cdot (4 \times 10^{-5})^2 = 8.6 \times 10^{-3} (\mu),$$

$$\delta y_{12} = -15.4 \times 10^3 \cdot (4 \times 10^{-5}) (3.3 \times 10^{-5})$$

$$= -18.8 \times 10^{-3} (\mu),$$

$$\text{and } \delta y_{22} = 3.5 \times 10^3 \cdot (3.3 \times 10^{-5})^2 = 3.2 \times 10^{-3} (\mu).$$

The contribution of the second order aberration to the image width is $3.1 \times 10^{-2} \mu$, so even in the ideal case of resolution of 7.5×10^5 , the ratio of the second order aberration to the image width is only 0.6×10^{-2} . When the energy and direction distributions of the doublet components are extremely different, the maximum error introduced by the second order aberration is as follows.

The error (the deviation of the doublet mass difference) is

$$\frac{3.6 \times 10^7}{7.5 \times 10^5} \times 0.6 \times 10^{-2} = 0.3 (\mu u),$$

where the mass is assigned to be 36 and the resolution is 7.5×10^5 .

In the digital peak matching method, the mismatching degree of 1/200 can be recognized and it corresponds to the mass of 0.5 μu in the above condition. And so, the error caused by the second order aberration must be investigated whether it exists or not.

2.2 Method of Doublet Mass Difference Determination

As mentioned above, the locating of mass peaks can be realized in the order of 1/100 peak width or somewhat better by the digital method used. In such case, the similarity between the peak shapes becomes one of the most important factors for the precise atomic mass determination in the

order of magnitude of 10^{-8} . If the peak shapes of doublet components are not similar within the order of 1/100 peak width with each other, the measured mass difference may depend on which points of the peaks are taken as their representative points.

In general, the ion beam of each doublet component has a different intensity distribution in direction and/or energy.

And in such case, the peak shapes are not similar with each other theoretically. The real dissimilarity between peak shapes may be due to the various causes, such as first order defocusing, second order aberration, ion intensity, small angle scattering etc. So, for the precise atomic mass determination with the accuracy of about 10^{-8} , it becomes very important to do the experimental investigations on the peak dissimilarity effect. According to such considerations, the following treatments were performed in this work for measuring the mismatching degree between the peaks of doublet components to be compared.

2.2.1 Matching Point Determination

In order to determine the most reliable mismatching degree of peaks to be compared, the following six treatments were investigated.

- 1) Linear moment (G_1)
- 2) Square moment (G_2)
- 3) Cubic moment (G_3)
- 4) Median (S)
- 5) Gaussian fitting (G)
- 6) Parabolic method (P)

The ion currents of the doublet to be compared were accumulated by a pulse height analyzer and the peak shape $f(X)$ could be known as a function of the channel number X .

1) Linear moment (G_1)

As the representative point of a peak, the linear moment G_1 defined as follows is employed.

$$G_1 = \frac{\sum X f(X)}{\sum f(X)} .$$

G_1 is what is called the first moment or the center of gravity of a mass peak.

The mismatching degree ΔG_1 of the doublet M and $M + \Delta M$ is expressed as

$$\Delta G_1 = G_{1(M)} - G_{1(M + \Delta M)} .$$

2) Square moment (G_2)

The representative point is expressed as

$$G_2 = \frac{\sum X^2 f(X)}{\sum f^2(X)} .$$

G_2 is different from what is called the second moment which is $\sum X^2 f(X) / \sum f(X)$, and G_2 gives the equal weight to all points of a mass peak.

The mismatching degree is obtained by

$$\Delta G_2 = G_{2(M)} - G_{2(M + \Delta M)} .$$

3) Cubic moment (G_3)

The representative point is expressed as

$$G_3 = \frac{\sum X^3 f(X)}{\sum f^3(X)} .$$

In this moment, the narrow top region of the mass peak is weighted compared to the cases of G_1 and G_2 . From the standpoint that the narrow top region of the mass peak must have the large weight, the cubic moment is the best one in G_1 , G_2 and G_3 , but from the viewpoint that all channels have equal weights, the square moment may be the best one.

The mismatching degree is obtained by

$$\Delta G_3 = G_{3(M)} - G_{3(M + \Delta M)} .$$

4) Median (S)

The median S is the channel number of the half area of the peak and is different from the linear moment G_1 . From experience, the following relation can be hold in M_0 (mode or top of the peak), S and G_1

$$\frac{M_0 - S}{S - G_1} \approx \frac{2}{1} .$$

The mismatching degree is obtained by

$$\Delta S = S_M - S_{M + \Delta M} .$$

5) Gaussian fitting (G)

The Gaussian curve is fitted to the mass peak to be measured, using the least squares treatment under the assumption that the mass peak has a Gaussian curve. The representative point G is given by the X coordinate of the Gaussian curve top. Figure 2 shows the plots of C_3 and C_2D_6 mass peaks and the error curves between the Gaussian curve and the mass peaks i. e., $A \cdot \exp[-H^2(X - X_0)^2] - f(X)$, calculated by a computer. The Y axis is normalized by A which is the maximum in the Gaussian curve.

As shown in Fig. 2, the mass peaks have slightly sharper top than the Gaussian curve, but the maximum difference between them is within 10 % of the peak height.

The mismatching degree is obtained by

$$\Delta G = G_M - G_{M + \Delta M} .$$

6) Parabolic method (P)

The parabolic method is not one which gives the representative point of the mass peak such as the above five methods, but one giving directly the mismatching degree of doublet peaks. To calculate the mismatching degree ΔI by this method, a quadratic function $A(I)$ is defined as follows:

Fig. 2. Plots of C_3 and C_2D_6 mass peaks and error curves between them and the Gaussian curve.

$$A(\Delta i) = \sum [f_M(X) - f_{M+\Delta M}(X + \Delta I - \Delta i)]^2.$$

The argument of this function $A(\Delta i)$ is expressed by channel numbers and corresponds to the supposed shift of a peak to the other one.

For small values of $(\Delta i - \Delta I)$, the function can be reduced to the parabolic form *versus* $(\Delta i - \Delta I)$ as shown in the following.

$$\begin{aligned} A(\Delta i) = & \sum [f_M(X) - f_{M+\Delta M}(X + \Delta I - \Delta i)]^2 \\ & - \sum [f_M(X) - f_{M+\Delta M}(X)]^2 - 2 \sum [f_M(X) \\ & - f_{M+\Delta M}(X)] f'_{M+\Delta M}(\Delta I - \Delta i) - \sum [f_M(X) \\ & - f_{M+\Delta M}(X)] f''_{M+\Delta M}(X) (\Delta I - \Delta i)^2 \\ & + \sum f_{M+\Delta M}^2(\Delta I - \Delta i)^2. \end{aligned}$$

The area of each peak is normalized, i. e., $\sum f_M(X) = \sum f_{M+\Delta M}(X)$ and the second and the third terms are zero, and finally we obtain

$$A(\Delta i) = \sum [\{f_M(X) - f_{M+\Delta M}(X)\}^2 + f'_{M+\Delta M}(X) \times (\Delta I - \Delta i)^2].$$

The minimum of $A(\Delta i)$ gives the degree of similarity between two peaks, and if the shapes of two peaks are quite similar $A(\Delta i)$ becomes zero. And the abscissa of the apex of this parabola corresponds to the mismatching degree between the peaks. Figure 3 shows an example of the parabola curve. The solid circles shown are the values calculated from $A(\Delta i)$ for certain ΔR and the solid curve was drawn by the least squares treatment.

Gaussian fitting and the parabolic method belong to the category of whole peak matching, while other treatments do to the peak top matching.

Fig. 3. An example of the parabolic curve.

Fig. 4. Plots of the representative points versus S_k .

In order to investigate the peak shape dependency of the mismatching degree calculated by the above six treatments for certain ΔR , the skewness S_k which represents the asymmetry of the peak shape is defined as

$$S_k = \frac{\varepsilon_3}{\sigma^3},$$

where $\sigma^3 = \Sigma f(X)(X - G_1)^3 / \Sigma f(X)$ and $\sigma^2 = \varepsilon_2 = \Sigma f(X)(X - G_1)^2 / \Sigma f(X)$.

Figure 4 shows the plots of the representative points calculated by the above treatments against S_k . G_3 was arbitrary chosen as a reference value. As seen in the figure, the values calculated from these treatments stand on a line and the channel difference between each treatment and G_3 is proportional to S_k .

Figure 5 shows the comparison among the mismatching degree obtained by the above treatments for a certain ΔR . The open circles on the upper horizontal line are the representative points of the C_3 peak displayed by the channel number. Those of the lower line are these points of the C_2D_6 peak. The gradient of each line

is the mismatching degree between two peaks calculated by each method. The channel differences of the parabolic method are shown in the same figure. It can be seen that the position of the representative points is greatly related with S_k .

The matching resistance ΔR_0 was calculated from the several sets of ΔR and the mismatching degree by a linear interpolation as shown in Fig. 6. The solid line is obtained from these five points by the least squares treatment. The representative point is the square moment in this case. Figure 7 shows the doublet mass differences of one run obtained from 1~6 treatments mentioned above. Upper group shows the mass differences of ($C_3-H^{35}Cl$). The error associated with each value is about $0.4 \mu u$ and the difference among each value is about $0.1 \mu u$. C_3 ion is a fragment ion produced from C_3H_4 . $H^{35}Cl$ ion is formed from the reaction in the ion source, and the sample gases used are trichloroethylene and allene. Therefore, the ion beams of C_3 and $H^{35}Cl$ have the possibility to have the different distribution of energy and direction with

Fig. 5. Comparison between the results calculated from 1~6 treatments for a certain ΔR .

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Fig. 6. An example of determining the mismatching resistance ΔR_0 .

Fig. 7. Comparison of the doublet mass differences obtained from 1~6 treatments.

each other. However, as seen in the figure, the results show the good agreement with- in the associated errors. Lower group shows the mass differences of $(\text{C}_2\text{D}_6 - \text{C}_3)$.

The C_2D_6 ion is the parent ion, while the C_3 ion is a fragment ion. And so, there also is the possibility to have the different distribution of energy and direction, but

the results show the good agreement. In Fig. 8 the doublet mass differences of ($C_3-H^{35}Cl$) obtained from 17 runs are shown. The open circles of the upper side show the measured mass differences calculated from the median method and in the lower side the differences between the values of the median and of the other treatments are shown. The lower scale is expanded by five times as compared with that of the upper one. The difference among one run in 1~6 treatments is smaller than that among many runs by about five times.

From the check mentioned above, it became clear that in the present case the difference of the peak shapes between the doublet components is not so large and does not introduce the systematic error

exceeding the statistical error in the measured mass differences, therefore, in the present case the median, which is most convenient in calculation, was adopted as the representative point of a peak.

2.2.2 One Matching Error

It has been reported that in the digital peak matching method the mismatching degree can be determined with the accuracy of about $1/100 \sim 1/1000$ of the peak width. However, this may depend on the instrumental and measuring stabilities. To test the reliability of one matching, the amount of the one matching error was estimated.

Figure 9 shows the mismatching degree for a certain ΔR . The peaks of the doublet were ^{37}Cl and $D^{35}Cl$ and the width of them was about 100 channels. The

Fig. 8. Comparison of the mass differences of ($C_3-H^{35}Cl$) obtained from 17 runs.

average mismatching degree was 1.491 channels and the statistical deviation was 1.000 channels and, therefore, the average one matching error is 1/100 of the peak width. If largely deviated ones in the both sides were rejected, the average mismatching degree was 1.498 channels and the statistical deviation was 0.711 channels. The fullwidth resolution was about 200,000, therefore, one channel corresponds to $1.9 \mu\text{u}$ at mass 37. If we adopted 10 pairs of ΔR in one run, it would be estimated that the error attached to the doublet mass difference was about $0.4 \sim 0.5 \mu\text{u}$. On the other hand, the error associated to the doublet mass difference of ($\text{D}^{35}\text{Cl}-^{37}\text{Cl}$) was $0.3 \sim 0.4 \mu\text{u}$ except some large ones.

The smoothness of the peaks may influence the scattering of the matching degree. In the present case, the counting rate of the top region of mass peaks was of the order of $10^2 \sim 10^3$ per one channel. If the counts of a certain channel is n , the statistical error will be about $\sqrt{n}$, but by 60Hz hum magnetic field it was greater by about three times than $\sqrt{n}$. The more counts of ions than certain extent did not increase the smoothness of peaks by such oscillation.

3. Results and Discussion

3.1 Doublet Mass Differences

In order to determine the atomic

masses of D, H, ^{35}Cl and ^{37}Cl as accurate as possible, the mass differences of the following doublets were measured.

These doublets were measured with the half height resolution of $300,000 \sim 500,000$. The gas samples used were as follows: ethylene ($\text{H}_2\text{C}=\text{CH}_2$) for the C_2H_4 ion; acetylene- d_2 ($\text{D}-\text{C}\equiv\text{C}-\text{D}$) for the C_2D_2 ion; allene ($\text{H}_2\text{C}=\text{C}=\text{CH}_2$) for C_3 and C_3H_2 ions; ethane- d_6 ($\text{D}_3\text{C}-\text{CD}_3$) for the C_2D_6 ion; trichloroethylene ($\text{H} \text{---} \text{C}=\text{CCl}_2$) for H^{35}Cl , ^{37}Cl and H^{37}Cl ions; the mixture of trichloroethylene and ethane- d_6 for the D^{37}Cl ion; propane ($\text{CH}_3-\text{CH}_2-\text{CH}_3$) for the C_3H_8 ion; allene- d_4 ($\text{D}_2\text{C}=\text{C}=\text{CD}_2$) for the C_3D_4 ion. The doublet mass differences of ($\text{C}_2\text{D}_6-\text{C}_3$) and ($\text{C}_3-\text{H}^{35}\text{Cl}$) reported in 1970 were measured with A-D converter mode and the other with pulse count mode.

Assuming that the mismatching degrees obtained for (ΔR), linearly correlate with these corresponding as $y = ax + b$ ($y = \text{channel difference}$; $x = \Delta R$), the matching resistance ΔR_0 was calculated using 10 points of ΔR in ordinary cases by the least squares method. The error attached to each ΔR_0 is calculated as follows:

Fig. 9. Distribution of channel differences at a certain ΔR .

$$\text{error} = e_0 \sqrt{\frac{\sum (\Delta R_i - \Delta R_0)^2}{D}} \div a,$$

$$\text{where } D = \begin{vmatrix} [\Delta R^2] & [\Delta R] \\ [\Delta R] & 1 \end{vmatrix}, \quad e_0 = \sqrt{\frac{\sum v_i^2}{n-1}},$$

and $v_i = (\text{channel differences at } \Delta R_i) - (a\Delta R_i + b)$.

In the ideal case, the doublet mass difference is calculated from $\Delta M = (\Delta V/V)M = (\Delta R_0/R)M$. In actual cases, this relation may not be always satisfied, so it is necessary to add the correction term to the above relation as follows:

$$\Delta M = \frac{\Delta V}{V} M = (1 + \epsilon) \frac{\Delta R_0}{R} M.$$

The correction factor ϵ was obtained from one hydrogen mass. The change of ϵ for a long period of time is shown in Fig. 10. As seen in the figure, ϵ gradually decreased from 3.2×10^{-5} to -6.0×10^{-5} .

Fig. 10. Change of ϵ for a long period of time.

But ϵ did not change largely during rather short time of period when the doublet mass difference measurements were carried out except in few cases. However, for the measurements at different mass numbers, some great change of the ϵ value was found. One of the causes of such a change might be ascribed to the charging up on the surfaces of analyzer electrodes and slit blades. The weak intensity of the ion current at the doublet mass difference measurement did not make the insulating films on these surfaces, but the strong intensity of ions made them when the objective peak was searched by changing the strength of the main magnet.

The ϵ correction has the following merits.

The measurement of the main bleeder resistance value is not necessary to know with the same accuracy of the variable resistance value. The effects of the charging up on the electrode surfaces and the slit blades and of small change of the stray field of an electric field by changing V , $V + \Delta V$ are included in the value ϵ . If ϵ is 1×10^{-5} and the doublet mass difference to be measured is 100 mu, the error of 1μ is introduced in the doublet mass difference.

In order to check the daily change of ϵ for a long period of time and the consistency in a long period between the different runs of the doublet mass difference measurement caused by changing of ϵ , the determination of the doublet mass difference ($C_2D_6 - C_3$) had been carried out through the period of about two months. The results obtained are shown in Fig. 11 and Table 1. The doublet mass differences measured during this period seem to be in rather good agreement with each other within the quoted errors of the mass differences. However, an example of the

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Fig. 11. Measured mass differences of ($\text{C}_2\text{D}_6-\text{C}_3$) for two months.

Table 1. Measured mass differences of ($\text{C}_2\text{D}_6-\text{C}_3$) for two months.

$\text{C}_2\text{D}_6-\text{C}_3$	Measured mass differences (μu)
Mar. 17	$84,612.36 \pm 0.24$
Apr. 14	$84,611.08 \pm 0.44$
Apr. 16	$84,610.90 \pm 0.37$
May 9	$84,611.57 \pm 0.42$
Average	$84,611.60 \pm 0.34$

systematic shift of measured mass differences which seems to be due to the change of ϵ is shown in Fig. 12. The mass differences measured in the period from Mar. 12 to Mar. 20 gradually increased, and after Mar. 22 they tended to a definite value. Therefore, for calculating the average of such doublet mass differences, the values from Mar. 12 to Mar. 20 were rejected.

Figures 13(a)~13(i) show the measured mass differences. As seen in the figures, these values are not always in agreement with each other within their errors. But in the present case, it is assumed that these are scattered by the statistical fluctuation and the average is calculated by the following equation.

Fig. 12. Systematic change of measured mass differences caused by the change of ϵ .

$$\Delta M(\text{average}) = \frac{\sum \Delta M_i \cdot \frac{1}{r_i}}{\sum \frac{1}{r_i}},$$

where ΔM_i is the measured mass difference and r_i is the error associated to ΔM_i in which as the weight the reciprocal of the error, not the square, associated to

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Fig. 13 (a). Mass differences of ($\text{H}^{35}\text{Cl}-\text{C}_3$) measured in 1970.

Fig. 13 (b). Mass differences of ($\text{H}^{35}\text{Cl}-\text{C}_2\text{D}_6$) measured in 1970.

each measured value was adopted. The error r for the average value obtained is calculated by the following equation.

$$r = \sqrt{\frac{\sum (\Delta M_i - \Delta M)^2}{n(n-1)}} \quad (1)$$

The results of these doublet mass differences are shown in Table 2. And

the errors quoted in the table are estimated as follows:

$$\text{quoted error} = \frac{\delta(\Delta R)}{R} M + \frac{\Delta R \cdot \delta(R)}{R^2} M,$$

where $\delta(\Delta R)$ is the sum of the errors of the resistance measurement of ΔR and the error of Eq. (1), and $\delta(R)$ is the sum of the errors caused by the resistance

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Fig. 13 (c). Measured mass differences of $(\text{C}_2\text{D}_6 - \text{C}_3)$.

Fig. 13 (d). Measured mass differences of $(\text{C}_3 - \text{H}^{35}\text{Cl})$.

Table 2. Measured doublet mass differences.

Doublet	Date	Mass No.	No. of measurement	Mass difference (μu)
$\text{C}_2\text{D}_6 - \text{C}_3$	'70	36	4	$84,611.600 \pm 0.340$
$\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}$	'70	36	9	$107,934.900 \pm 0.540$
$\text{C}_3 - \text{H}^{35}\text{Cl}$	'70	36	6	$23,321.830 \pm 0.630$
$\text{C}_2\text{D}_6 - \text{C}_3$	'70-'71	36	10	$84,611.730 \pm 0.411$
$\text{C}_3 - \text{H}^{35}\text{Cl}$	'71	36	13	$23,322.328 \pm 0.325$
$\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}$	'71	36	11	$107,933.422 \pm 0.538$
$\text{C}_3\text{H}_2 - \text{H}^{37}\text{Cl}$	'71	38	14	$41,922.176 \pm 0.305$
$\text{D}^{35}\text{Cl} - ^{37}\text{Cl}$	'71	37	14	$17,051.816 \pm 0.185$
$\text{C}_2\text{H}_4 - \text{C}_2\text{D}_2$	'71	28	16	$3,096.444 \pm 0.127$
$\text{C}_3\text{H}_8 - \text{C}_3\text{D}_4$	'71	44	8	$6,192.705 \pm 0.265$

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Fig. 13 (e). Measured mass differences of $(C_2D_6-H^{35}Cl)$.

Fig. 13 (f). Measured mass differences of $(C_3H_2-H^{37}Cl)$.

measurement of $R_H(\Delta R$ for the hydrogen check) and by the hydrogen check.

The zero cycle check for doublet pairs is done at mass 36. The closure error in this case is

$$\delta = [\Delta M(C_2D_6-H^{35}Cl) - \Delta M(C_2D_6-C_3) - \Delta M(C_3-H^{35}Cl)].$$

This closure error δ calculated from the

mass differences measured in 1970 was $1.47 \mu u$ and that measured in 1971 is $0.636 \mu u$. Error of $1.47 \mu u$ in 1970 exceeded that estimated from the quoted errors of each doublet, therefore, these doublet mass differences might have some errors. To find out which doublet mass difference value is in error, these mass differences were remeasured and δ of

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Fig. 13 (g). Measured mass differences of ($\text{D}^{35}\text{Cl} - ^{37}\text{Cl}$).

Fig. 13 (h). Measured mass differences of ($\text{C}_2\text{H}_4 - \text{C}_2\text{D}_2$).

0.636 μu was obtained from these re-measured doublet values. This closure error seems to be consist with the quoted errors of these doublet values. And it was also found that the agreement between the doublet ($\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}$) values of 1970 and 1971 is bad. So, it may be able to conclude that the 1970 ($\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}$) value

must be in error.

In the previous work, the visual peak matching was adopted and the following relation was used to calculate the mass differences from the measured ($\Delta R/R$) for doublets;

$$\Delta M = (1 + \epsilon) \frac{\Delta R}{R} M + dM \quad \text{or} \quad \frac{\Delta M}{M} = (1 + \epsilon) \frac{\Delta R}{R} + d$$

Fig. 13 (i). Measured mass differences of ($C_3H_8-C_3D_4$).

In the previous case, the second correction term dM in the above relation was estimated to be $0.26 \mu u$. When such correction is necessary, the consistency factor g calculated as the ratio of external and internal errors must be considerably larger than 1. In the present case, however, this g was estimated rather small, as shown in later. Consequently, this correction term was neglected here.

3.2 Masses of H, D, ^{35}Cl , ^{37}Cl , ^{16}O and ^{14}N

In order to calculate the masses of H, D, ^{35}Cl and ^{37}Cl from all doublet mass differences measured, the least squares treatment was adopted. The input data are shown in Table 2. The doublet mass difference of ($C_2D_6-H^{35}Cl$) ($=107,934.90 \pm 0.54 \mu u$) was rejected in the calculation, according to the reason mentioned above. The mass excesses thus calculated are shown in Table 3. In this calculation, the error attached to each doublet mass difference was used as the weight.

For investigating the reliability of these results, the consistency factor g was calculated as follows:

Table 3. Mass Excesses of H, D, ^{35}Cl and ^{37}Cl .

	Mass excess (μu)	External error	Internal error
H	7,825.065	0.015	0.030
D	14,101.930	0.020	0.040
^{35}Cl	-31,147.21	0.10	0.20
^{37}Cl	-34,097.10	0.11	0.22

$$g = \left[\frac{\sum (p v v)}{N - n} \right]^{1/2},$$

where N is the number of doublets, n is the number of unknowns, p is the weight attached to each doublet mass difference, and v is the residual of each doublet mass difference. This g seems to be considerably smaller than that expected when doublet mass differences measured are in the statistical distribution. One of the reasons of this fact may come from that the error caused by the small change of c is doubly considered in $\delta(\Delta R)$ and $\delta(R)$. If we neglect the error which comes from $\delta(R)$, g is 0.8 in the least squares calculation. It may be reliable that the error of $\delta(R)$ is taken into consideration, but the amount of this error can not be

estimated reliably. So in the present case, the internal errors are adopted as the final errors to be attached to the calculated atomic masses. g of 0.8 shows that the error of d type may not exist and even if exists, it may be able to neglect in the present calculation of doublet mass differences.

From these errors, the accuracy of presently determined masses is estimated to be from 6×10^{-9} to 3×10^{-8} .

Using the mass of H obtained and the doublet mass differences, which were previously reported, of

$$(\text{C}_2\text{H}_4 - ^{14}\text{N}_2) = 25,152.44 \pm 0.19 \mu\text{u}$$

$$\text{and } (\text{C}_2\text{H}_4 - \text{C}^{16}\text{O}) = 36,384.01 \pm 0.24 \mu\text{u},$$

the masses of ^{14}N and ^{16}O were obtained to be

$$^{14}\text{N} = 14 \text{ u} + 3,073.91 \pm 0.14 \mu\text{u}$$

$$\text{and } ^{16}\text{O} = 16 \text{ u} - 5,085.75 \pm 0.25 \mu\text{u}.$$

3.3 Discussion

In Figs. 14(a)~14(f) and Tables 4(a) and 4 (b), the comparison between the present results and others' and the 1964 and 1971 mass table values are shown. The comparison of the mass differences of (H_2 -D)

Fig. 14 (a). Comparison of the present results of H with others.

Fig. 14 (b). Comparison of the present results of D with others.

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Fig. 14 (c). Comparison of the present results of ^{35}Cl with others.

Fig. 14 (d). Comparison of the present results of ^{37}Cl with others.

and $2-(^{37}\text{Cl}-^{35}\text{Cl})$ are shown in Figs. 15 (a) and 15 (b), and Table 5.

The masses of H reported so far are in rather good agreement within the quoted errors, except the Minnesota'57 and '66 values. And the inconsistency existing in the 1950's between the masses of H seems to be considerably improved. The present value of D agrees well with our 1970 value (Osaka'70) and the values of Argonne and Brookhaven, and the Minnesota'56 value. But it does not agree

with Princeton'70, Osaka-GE. ED. '69 and Minnesota '67 values. And in general the consistency among the masses of D so far reported seems to be worse than the case of H. As to the mass of ^{35}Cl , the present value well agrees with almost values except the values of Harvard '65 and one of our '70. Two ^{35}Cl values preliminary reported by us in 1970 are different with each other as seen in Fig. 14 (c). These masses were calculated by using the doublets ($\text{C}_3\text{-H}^{35}\text{Cl}$) and

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^{16}O

Fig. 14 (e). Comparison of the present results of ^{16}O with others.

^{14}N

Fig. 14 (f). Comparison of the present results of ^{14}N with others.

($\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}$) measured in 1970 as follows.

$$M(^{35}\text{Cl}) = \Delta M(\text{C}_3 - \text{H}^{35}\text{Cl}) - M(\text{H}) + 36 \quad (\text{A})$$

$$M(^{35}\text{Cl}) = \Delta M(\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}) + M(\text{C}_2\text{D}_6) - M(\text{H}) \quad (\text{B})$$

As mentioned above, by remeasuring these mass differences, it became clear that the doublet mass difference of ($\text{C}_2\text{D}_6 - \text{H}^{35}\text{Cl}$) must have some errors and, therefore, the mass calculated using Eq. (B) may be in error. Consequently, the mass of ^{35}Cl having the mass excess of $-31,148.30$

systematically deviates. The present value of ^{37}Cl agrees with the values at Argonne and Minnesota, but it does not agree with the values at Harvard and Princeton. Harvard value deviates to low mass side by two times of its error from other mass spectroscopic values. The present value of ^{14}N agrees with the values of Brookhaven '58 and Princeton '70, but it does not agree with the values of Minnesota '56 and Brookhaven '59.

For the mass differences such as

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Table 4 (a). Comparison of the present results of H, D, ^{35}Cl and ^{37}Cl with others (unit: μu).

	H	D	^{35}Cl	^{37}Cl
Brookhaven '58 ⁴⁾	7824.958 $\pm$ 87	14101.834 $\pm$ 103		
Brookhaven '59 ⁵⁾	7825.928 $\pm$ 278	14103.348 $\pm$ 370		
Harvard '65 ⁶⁾			-31148.620 $\pm$ 680	-34099.730 $\pm$ 950
Minnesota '56 ^{7) 8)}		14102.118 $\pm$ 556		
Minnesota '57 ⁹⁾	7824.663 $\pm$ 200			
Minnesota '58 ¹⁰⁾			-31146.300 $\pm$ 1900	-34096.000 $\pm$ 1600
Minnesota '66 ¹¹⁾	7825.220 $\pm$ 30		-31146.400 $\pm$ 600	-34096.700 $\pm$ 600
Minnesota '67 ¹²⁾		14102.220 $\pm$ 078		
Argonne '67 ¹³⁾	7825.010 $\pm$ 028	14101.887 $\pm$ 27		
Argonne '69 ¹⁴⁾	7825.055 $\pm$ 40	14101.760 $\pm$ 200	-31147.250 $\pm$ 300	-34096.660 $\pm$ 300
Osaka (GE. ED.) '68 ¹⁵⁾	7824.990 $\pm$ 140			-34096.700 $\pm$ 600
Osaka (GE. ED.) '69 ¹⁶⁾		14101.640 $\pm$ 150		
Osaka '70 ³⁾	7825.005 $\pm$ 49	14101.933 $\pm$ 57	{ -31146.830 $\pm$ 640 -31148.300 $\pm$ 640	
Princeton '70 ¹⁸⁾	7825.029 $\pm$ 5	14101.771 $\pm$ 10		-34097.575 $\pm$ 56
Mass Table '64 ¹⁹⁾	7825.190 $\pm$ 80	14102.220 $\pm$ 120	-31148.900 $\pm$ 1300	-34101.500 $\pm$ 1100
Mass Table '71 ²⁰⁾	7825.220 $\pm$ 40	14102.220 $\pm$ 70	-31146.410 $\pm$ 330	-34096.960 $\pm$ 270
Present value	7825.065 $\pm$ 30	14101.930 $\pm$ 40	-31147.210 $\pm$ 200	-34097.100 $\pm$ 220

Table.4 (b). Comparison of the present results of ^{16}O and ^{14}N with others (unit: μu).

	^{16}O	^{14}N
Brookhaven '58 ⁴⁾	-5086.049 $\pm$ 345	3074.314 $\pm$ 200
Brookhaven '59 ⁵⁾	-5087.046 $\pm$ 1140	3074.878 $\pm$ 515
Minnesota '56 ^{6) 7)}		3073.487 $\pm$ 270
Minnesota '57 ⁹⁾	-5085.850 $\pm$ 533	
Osaka (GE. ED.) '68 ¹⁵⁾	-5087.900 $\pm$ 1200	
Princeton '70 ¹⁸⁾	-5085.567 $\pm$ 26	3073.973 $\pm$ 14
Mass Table '64 ¹⁹⁾	-5084.890 $\pm$ 280	3074.390 $\pm$ 170
Mass Table '71 ²⁰⁾	-5084.980 $\pm$ 200	3074.400 $\pm$ 360
Present value	-5085.750 $\pm$ 250	3073.910 $\pm$ 140

(H_2 -D) and (^{37}Cl - ^{35}Cl), the consistency between them reported so far, including the author's, seems to be almost satisfactory. As seen in Fig. 15 (a), the present value of (H_2 -D) calculated from (C_3H_8 - C_3D_4) and (C_2H_4 - C_2D_2) is in good agreement with others' even in rather small errors quoted. The old values of Minnesota '56 and Harvard '63 seem to deviate to small

direction. As for the mass difference between Cl-isotopes (^{37}Cl - ^{35}Cl), at 1963 Vienna Conference Duckworth pointed out the importance of this mass difference relating to the determination of the separation energy of last two neutrons of nuclei in the heavy mass region. Since then, the measurements have been reported by several authors. Though the scattering of

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Fig. 15 (a). Comparison of the present results of the doublet mass difference of ($\text{H}_2\text{-D}$) with others.

Fig. 15 (b). Comparison of the present results of the doublet mass difference of $2-(^{37}\text{Cl}-^{35}\text{Cl})$ with others.

mass values of each isotope is fairly large as seen above, the differences of them are not so bad. However, the so-called mass table values of this mass difference appeared in 1964-Table and even in the recent 1971-Table must be in error.

Recently L. G. Smith in Princeton reported six light masses with extremely high accuracy. In his case, the principle of the doublet mass difference measure-

ment is quite different from others. As well known, the apparatus used is one of the resonance type mass spectrometer and doublet mass differences are calculated from the differences of the resonance frequency of each doublet component. The frequency measurement can be done with very high accuracy in general. To determine the atomic masses, he used many kinds of doublets involving the

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Table 5. Comparison of the present results of (H_2 -D) and $2-(^{37}Cl-^{35}Cl)$ with others (unit: μu).

	(H_2 -D)	$2-(^{37}Cl-^{35}Cl)$
Minnesota '56 ⁷⁾	1547.210 $\pm$ 400	
Minnesota '58 ¹⁰⁾		2949.700 $\pm$ 2500
Minnesota '66 ¹¹⁾		2950.300 $\pm$ 600
Minnesota '67 ¹²⁾	1548.220 $\pm$ 50	
Brookhaven '58 ⁴⁾	1548.081 $\pm$ 82	
Brookhaven '58 ¹⁷⁾	1548.780 $\pm$ 180	
Harvard '63 ²¹⁾	1547.770 $\pm$ 280	
Harvard '65 ⁶⁾		2951.110 $\pm$ 590
Argonne '67 ¹³⁾	1548.070 $\pm$ 80	
Argonne '69 ¹⁴⁾	1548.350 $\pm$ 208	2949.410 $\pm$ 420
Osaka (GE. ED.) '69 ¹⁶⁾	1548.210 $\pm$ 600	
Osaka '69 ¹⁾	1548.081 $\pm$ 80	
Princeton '70 ¹⁸⁾	1548.287 $\pm$ 4	2950.290 $\pm$ 63.
Mass Table '64 ¹⁹⁾	1548.160 $\pm$ 140	2952.600 $\pm$ 1700
Mass Table '71 ²⁰⁾	1548.220 $\pm$ 80	2950.550 $\pm$ 430
Present (adjusted) value	1548.196 $\pm$ 58	2949.890 $\pm$ 300
($C_2H_4-C_2D_2$)/2	1548.222 $\pm$ 73	
($C_3H_8-C_3D_4$)/4	1548.176 $\pm$ 133	

nuclides concerning, and carried out the numerous numbers of measurements of each doublet. For calculating the masses from these measured doublet mass differences, the least squares treatment was adopted. As the results of such experimental procedures, the attached errors to the final mass values become to be extremely small ones. And the accuracy of atomic masses reported can be estimated to be in the order of magnitude of 10^{-9} . It may have some meanings to compare the author's present results, which are determined by an ordinary method using a static type machine, with the Smith's dynamic results. As seen in the tables and figures shown above, for H, ^{35}Cl , (H_2 -D), ($^{35}Cl-^{37}Cl$), ^{14}N and ^{16}O , the present values are in good agreement with the Smith's values within the Smith's

small errors. However, D and ^{37}Cl are not in agreement with each other.

In the determination of atomic masses with the absolute accuracy of $10^{-8}\sim 10^{-9}$, many further careful investigations to do, especially relating to various systematic errors, are still remained.

Finally, it may be necessary to touch on the so-called "Table value" of atomic masses. As seen in the figures shown above, the Table values are deviated unidirectionally against almost all mass spectroscopic ones. Such serious fact is also found in the latest Mass Table published in 1971. The cause for such discrepancy has not yet been clear. But one reason must be due to that the recent mass spectroscopic data have not yet been adopted as input data of the least squares calculations when compiling the Table.

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