Present Status of the Two Stage Double Focusing Mass Spectroscope at Osaka University

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With the intention to determine the atomic masses in the accuracy up to the order of magnitude of $10^{-9}$, in 1967 we were planning to construct a new large tandem type mass spectroscope. The machine consists of two sets of first order double focusing mass analyzer. The first stage of the machine has a cylindrical electric field and a uniform magnetic field. The radii and the angles of these fields are 310 cm, 73.8° and 260 cm, 106.2° respectively. In the second stage, a uniform magnetic field is followed by a cylindrical electric one and the radius and the angle of the former field are 110 cm, 100° and those of the latter 310 cm, 80°. The two sets of analyzers are connected in inverse S-shape and an intermediate double focus-point is located between them. The total ion path length is about 37 m.

The calculated mass dispersion for 1% mass difference is about 35 cm and the resolution is calculated to be about $9.2 \times 10^6$ with 1 μm main slit width.

Till late spring of 1969, the machining work of the main parts of the machine was finished. Then the preliminary setting work was begun and in the middle of 1972 we succeeded in catching the first ion beam at the final focus-point. The mass dispersion at that time could be estimated to be nearly the expected value. However, the aspect of ion beam convergency was extremely far from the expected one. After several trials for focus adjustment of the machine as a whole, it was found that such work was seriously difficult in the preliminary stage of the adjustment. So, since 1973, we had been carrying out the focus adjustment by using on the first stage analyzer at the intermediate focus-point.

After rather long investigations, it was found that the focusing properties depended critically on the location of ion beam in the magnetic field. Recently the focus adjustment work was finished and in the best condition the resolution of 800,000 or somewhat better could be attained.

Following to the above focus adjustment work, the doublet mass difference measurements were begun by the digital peak matching method at mass 28 and 36. And some atomic masses were calculated from the doublet mass differences.

The results obtained are as follows: $7,825.050 \pm 35 \, \mu u$, $D = 14,101.912 \pm 67 \, \mu u$, $N = 3,074.075 \pm 115 \, \mu u$ and $O = -5,085.281 \pm 307 \, \mu u$.

1. Introduction

In the precise determination of the fundamental physical quantities such as the atomic masses, nothing to say, the most important thing is in obtaining the results with the high accuracy as much as possible in the absolute sense not in the appearing one. In order to realize this purpose, many mass spectrosocists have been developing their instruments and measuring techniques. And they have been spending their efforts to find out the causes of systematic errors and to eliminate them as

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much as possible.

The highest accuracy so far obtained is that of L. G. Smith’s measurements\textsuperscript{3,4}. His instrument was a dynamic type mass spectrometer, “mass synchrometer”, and measuring technique was the so-called peak matching method developed by himself in 1953\textsuperscript{9}. The measuring accuracy appeared in his last work is estimated to be a few parts in 10\textsuperscript{7}. And the accuracies of other authors’ results are mostly in the order of magnitude of 10\textsuperscript{-8}.

However, unfortunately the inconsistency between the atomic mass values reported by several authors still remains and even in the most important mass standards such as H, D and \textsuperscript{35,37}Cl. And also the values appeared in the mass tables of 1964 and 1971 published by Wapstra et al. have the disagreement beyond the quoted errors with each author\textsuperscript{6,7}. Moreover the discrepancy between the mass spectroscopic values and the calculated masses in these mass tables seems to be greater than that among the mass spectroscopic values so far obtained.

Such unsatisfactory status in the measured atomic masses must come from several systematic errors existing in their instruments and measuring techniques. So still at the present the most important work to do in the precise atomic mass measurements is undoubtfully the convincing systematic error investigations.

In order to improve the difficulties above mentioned, the authors were intending to construct a new mass spectroscope with very large mass dispersion and high resolution and to determine the atomic masses in an absolute accuracy of 10\textsuperscript{-9}. In 1967, the basic calculation of the machine was begun and recently the first and preliminary results were obtained. In this paper, the general characteristics of the new mass spectroscope, the focusing property and some atomic masses preliminary obtained will be reported.

2. Instrumentation

2.1 Basic Consideration

As the type of the mass spectroscope newly constructed, by which we could determine the atomic masses with an accuracy of the order of magnitude of 10\textsuperscript{-9}, a large first order one directional double focusing machine of tandem type was adopted. The machine consists of two sets of a double focusing mass spectroscope and each of them has a cylindrical electric field and uniform magnetic field. These sets are connected in inverse S-shape and an intermediate double focus point is located between them. And the incident and exit angles of ion beam to the fields are vertical.

The reasons for adoption of the above type as that of the new machine were as follows: The authors would like to realize their intention surely and safely as much as possible and they were planning to construct a new mass spectroscope having the extremely large mass dispersion and the properly high resolution. In such case, the dimensions of the machine would become necessarily large. From the consideration on the machining and setting precision, it may be easier for the present purpose to adopt the cylindrical type for electric field and the uniform one for magnetic field and to use them in vertical ion injection and ejection than in the case of other type. On the other hand, from the limitation of the dimensions and precisions of the machine tools and the restriction of the space and shape of the room storing the mass spectroscope, it was difficult to achieve our purpose by a single stage type because of its too large dimension.

According to those considerations, the construction of a two-stage mass spectroscope having the first order one directional double focusing character was decided in 1967.
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As for the measuring techniques of doublet mass differences, the digital peak matching one was adopted. With this method it is not so difficult to detect the amount of peak-shift by one thousandth of peak width. So, when the measuring accuracy of $10^{-9}$ is required, the fractional mass difference for one peak width must be $10^{-6}$. If wishing to say in terms of “resolution”, the necessary resolution is $1 \times 10^6$.

When the image width is assumed to be $5 \mu m$, the mass dispersion for 1% mass difference must be designed to be $30 \text{ mm}$ in minimum.

However in the practical case, there are various causes on focus defects, so the designed values of mass dispersion and resolution must be several times of the above values.

For the tandem machine having four fields such as the type mentioned above the numbers of ion optical parameters are twenty and there are ten equations for focusing conditions. In the present, ten of these parameters were selected properly so that the machine could have the large mass dispersion and resolution as much as possible under the many restriction such as above mentioned.

After several numerical calculations, the characteristics of the new mass spectroscope constructed were determined as shown in Table 1. In the table, the calculated mass dispersion and resolution are also shown.

In Fig. 1 the schematic diagram of the machine is shown and its focusing characteristics can be seen in Fig. 2. In Fig. 3 the general view of the instrument is shown.

### 2.2 Ion source and main slit assembly

The ion source is a kind of low voltage arc type with axial magnetic field and its cross section is shown in Fig. 4. Ion extracted through a $1.5 \text{ mm}$ diameter circular hole are focused roughly on the main slit by an immersion lens for extraction and acceleration and an einzel lens of $50 \text{ mm}$ diameter. The focusing condition on the main slit is adjusted by supplying adequate potential to the immersion lens and the einzel lens. The distance between the ionization chamber and the immersion lens can be adjusted by two sets of screws or compressed oil. The converging rate, the direction and the profile of the ion beam seriously depend on the distance between them, so fine adjustment of ion beam conditions can be more easily done by the supply voltage of the immersion lens. The operational condition in long distance between the ionization chamber and the immersion lens is nearly equivalent to that in low potential between them. The potentials for these electrodes are supplied from the resistance bleeder shown in Fig. 5. All resistors are installed in a box in which freon gas is filled to prevent corona discharge.

The ion source assembly can be slided to horizontal and vertical directions by screws and the direction of ion beam also can be adjustable mechanically. The fine adjustment of ion beam direction to the main slit is done by supplying the potential to two sets of parallel plates which follow the einzel lens.

The operational condition of the ion source is as follows: The emission current stabilized is

### Table 1. Dimensions and ion optical parameters of the two stage double focusing mass spectrometer.

<table>
<thead>
<tr>
<th>Condition</th>
<th>E₁</th>
<th>H₁</th>
<th>H₂</th>
<th>E₂</th>
</tr>
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<tr>
<td>Final focusing point</td>
<td>a</td>
<td>310 cm</td>
<td>260 cm</td>
<td>110 cm</td>
</tr>
<tr>
<td>Dispersion for 1% mass difference</td>
<td>D% = 34.9 cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total magnification</td>
<td>G₁</td>
<td>0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution (1 µ main slit)</td>
<td>R₁max = 7.8 × 10⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total ion path</td>
<td>L = 37.3 m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intermediate focusing point</td>
<td>a'</td>
<td>850 cm</td>
<td>57 cm</td>
<td>19 cm</td>
</tr>
<tr>
<td>Dispersion for 1% mass difference</td>
<td>D₁ = 4.0 cm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnification</td>
<td>G₁</td>
<td>0.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Resolution (1 µ main slit)</td>
<td>R₁max = 7.8 × 10⁶</td>
<td></td>
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</tr>
</tbody>
</table>
Fig. 1. Schematic diagram of the machine. 1; ion source, 2; first electric field, 3; first magnetic field, 4; second magnetic field, 5; second electric field, 6; final focus point.
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Fig. 2. Focusing characteristics of the two stage double focusing mass spectrometer.

Fig. 3. General view of the instrument
Fig. 4. Cross section of the ion source. The diameter of the lens electrodes was reduced to 50 mm from 60 mm to prevent from breakdown.

Fig. 5. Resistance bleeder for lens electrodes. The circuit for peak matching is not used in present case.
about 20 mA and the ion current extracted from the ion source is 30–60 μA in the typical operation. The pressure in discharge chamber is of the order of 10\(^{-4}\) Torr. A filament is 0.3 mm tungsten wire and its current is about 7 A and supplied from two 220Ah-6 V lead storage batteries. The electron accelerating potential is 100 V which is supplied from 5Ah batteries. Gas sample reservoirs, needle valves, emission stabilizer and the batteries are mounted on a box of high voltage side and the emission current and the sample gas pressure in the ion source are controlled from ground through teflon rods.

The high voltage regulator for ion acceleration has a following character which was described in elsewhere in details:

- Voltage: 3~10\(\times\)10\(^4\) V
- Max. current: 2.5 mA
- D. c. stability: 1\(\times\)10\(^{-5}\)/min.

In the typical operation, the ion acceleration potential is about 50 kV.

The main slit assembly consists of a shutter, a z-slit, a main slit and a monitor. The shutter is insulated from ground potential and the total current extracted from the ion source is easily measured. The z-slit is a baffle of about 0.2 mm and movable to vertical direction ±5 mm. It defines the vertical position of ion beam at the main slit. The main slit consists of two stainless steel wire of 1 mm and aluminum foil of 10 μm is put between them. The width is continuously variable from its maximum to zero by rotating it around vertical axis at the center of it from outside the vacuum envelope. The inclination of the main slit can be also adjustable from outside. The monitor for measuring the ion current through the main slit is located just behind it.

The main slit and the ion source assembly can be moved to horizontal and vertical direction as a whole and the ion beam direction also adjustable by the same mechanism of the ion source. In order to easily adjust the position and direction of ion beam against the analyzing fields, the whole ion source assembly is counterbalanced by proper weights.

2.3 Electric field

The first and the second electric fields have similar construction except for their deflection angles and so the deflecting potential can be supplied simultaneously to the electrodes of these two electric fields by one voltage divider and the doublet mass differences can be measured by peak matching method. They are cylindrical type and the radius of central ion path is 310 cm. The deflection angle of the first electric field is 73.8° and the second one is 80°. These cylindrical electrodes are made of non-magnetic stainless steel, which are 25 mm sheets and welded by heric arc as shown in Fig. 6. Each of them is 30 cm high by 18 cm wide and the gap spacing is 50 mm which is maintained by the insulating spacers.

![Fig. 6. Photograph of the electrodes of electric analyzer.](image-url)
There are two auxiliary electrodes placed above and below the gap in each field, and field shape can be slightly and finely changed by supplying the small potential to them. In spite of the zero potential of the auxiliary electrodes, the field shape is slightly deviated from the ideal-cylindrical one at the center of the field by the influence of short height of the condenser electrodes and of the circular arc curvature.

The field defining plates are placed at the entrance and the exit of the fields to adjust the effective field boundaries. The direction and the energy defining slits are located at the entrance and the exit of the fields respectively. They can be moved to lateral direction by the micrometer screws and their width is continuously variable from zero to 5 mm with the reproducibility of 0.01 mm. The z-defining slits are also located at both sides of the fields and they are moved by screws continuously.

Each of the electric fields is mounted on a iron table which can be shifted in any directions including horizontal and vertical ones by ±50 mm and the horizontal adjustment is done by three oil and screw jacks.

The carefully stabilized voltage is supplied to the electrodes of the energy selector through the resistance network. The voltage source is eighteen 90 V dry batteries and the stability of few parts of $10^7$/min. is obtained by the stabilizing circuit which is similar one described in elsewhere. Fig. 7 and 8 show the photographs of the first and the second electric fields.

2.4 Magnetic field

The first and the second magnetic fields are of uniform ones whose radii of the central curvature are 260 cm and 110 cm respectively. The deflection angles of the first and the second fields are $106.2^\circ$ and $100^\circ$. The gap distance of the poles of both magnet are the same 12 mm, which are maintained by stainless steel spacers.
Because of smaller curvature of the ion path in the second magnetic field, the field strength of the second magnet becomes to be 2.4 times higher than that of the first one for deflecting the same ion beam and so the cross section of the yoke and core of the second magnet is made larger correspondingly than those of the first ones, for avoiding the saturation of the magnetic flux when measuring heavy masses.

The exciting coil of the magnets consists of a main and an auxiliary coils. The main coil of the first magnet is 1000 turns with the total resistance of 63 $\Omega$. The second one consists of two coils with 1240 turns, 43.7 $\Omega$. The auxiliary coils of both magnets consist of four coils with 20, 16, 11 and 11 turns respectively. The small correction of the field strength and drift can be adjusted by controlling the current of the auxiliary coils.

The coil current of each magnet is supplied by 2 V-225 Ah × 136 lead storage batteries and stabilized by a similar circuit shown in elsewhere. The drift in the field strength less than $5 \times 10^{-7}$/min. can be achieved by this circuit.

There are three ion monitors placed near the entrance, the exit and the center in the first magnet. They are 6 mm copper rods which can be moved to radial direction from outside of the vacuum envelope. The radial position as well as horizontal one of the ion beam in the magnet can be easily known by those devices.

The strength of the magnetic field can be measured by the hall element placed in the pole gap with the accuracy of better than $10^{-4}$. With the help of this circuit, the ion beam can be easily placed nearly on the collector slit.

Each of the magnets is placed on the twofold iron tables. The lower one is similar to that of the electric field and movable to any direction. The upper one can be moved by ±20 mm in the direction of radial symmetry line and the radius of the central ion path in the magnet can be changed. The total weights, including the tables, of the first and the second magnets are 13.2 and 11.7 ton.

The photographs of the first and the second magnets are shown in Fig. 11 and 12.

2.5 Collector slit and ion detection system

The ion measuring assembly at the intermediate focus-pointe consists of a collector slit, an ion current measuring system and a
photographic plate holder. They are mounted on an iron bench and can be moved ±40 mm in lateral direction and ±150 mm to the parallel direction of the ion beam by mean of the bellow and the vacuum-tight cylindrical tube. The vertical movement can be adjusted by four screws. And so, if the double focus-point exists in the region of the movable area of the collector slit, it can be easily located on the focus-point.

The collector slit has a shape of knife edge and its width from zero to 0.5 mm, inclination and rateral position can be adjusted by ±2 mm from outside of the vacuum chamber.

Followed the collector slit, there is a secondary electron multiplier of 16 stages and the gain of it is estimated to be about $10^6$ at the supply voltage of 2.5 kV.

The output from the secondary electron multiplier is fed to a d.c. amplifier or a pulse amp. commercially available. The input resistance of the d.c. amp. is $10^9 \Omega$.

The photographic plate can be mounted before the collector slit without breaking the vacuum system. It can be moved perpendicularly out of the vacuum chamber, and in the case of the electric detection it is located in the lower part and in photographic detection it can be elevated to the proper position.

2.6 Evacuating system

The vacuum envelope except for the ion source are made of iron to prevent stray magnetic hum field from penetrating to the ion path. Four gate values are installed as shown in Fig. 13 to evacuate each part independently. For evacuating the whole system, 15 sets of 6"-2" oil diffusion pumps are used and two 4" diffusion pumps are for the ion source and the main slit assembly. The 3" rough vacuum line for each pump set is centralized to a low vacuum tank which is evacuated by a set of 4" oil diffusion and rotary pump. Other 2" vacuum line for roughly evacuating each part runs parallel to the 3" line. It is evacuated by a mechanical booster and a 300 litter rotary pumps. To prevent from oil back diffusion, a liquid nitrogen trap is located between each pump and vacuum envelope. The vacuum is estimated to be in the range of $10^{-7}$ Torr. in the analyzing parts.

3. Focus Property

In the middle of 1972, we succeeded in the detection of ion beam at the final focus-point, but unfortunately the image was seriously distorted and the convergency of ion beam was disturbed. After several trials of the focus adjustment as a whole, it was found that such work was seriously difficult in the preliminary stages of the adjustment and so we had been carrying out the focus adjustment at the intermediate double focus-point as a first stage of the focus adjustment. The image profile at
this point also seemed to be distorted, but the image distortion was not so clearly observed on a CRT screen because of the electric detection.

To make clear the image profile and to search the ion beam focus property, the photographic detection and some devices for electric detection were used. The merit of the photographic detection is that we can see the image profiles of spectral lines directly on the photographic plates. If the operational conditions or the ion paths in the fields are changed the image profiles and converging rate of the ion beam will change, but the influences and effects to the image shapes by these changes can not be detected simultaneously by the photographic detection. On the contrary, with the electric detection the effects and the influences can be detected simultaneously but the image shape is not seen. To combine the merits of both detections, a pairs of parallel plates deflecting an ion beam vertically was installed behind the exit of the first magnetic field. A staircase voltage is supplied to one of the plates, of which voltage has a repeating period consisting of four steps, each step synchronized with the saw tooth voltage for scanning ion beam horizontally. We can see on a long-persistent CRT screen four ion beam peak traces representing the corresponding image profiles at four points along an image line as shown in Fig. 14 and 15, in which one
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Fig. 14. Image profiles taken by electric method with ion beam having different incident angles to the magnetic field. Two profiles in each figure are those taken by changing their energy by the fractional amount of two parts in 10^4.

Fig. 15. Image profiles of (C_2H_4-C_2D_2) doublet taken with the diversent angle defining slit which was deviated into two parts by 0.3 mm tungsten wire.

step corresponds to 0.5 mm along an image length. Comparing the ion peak traces to the photographs taken with the same condition, we can know the image profiles from newly observed peak traces and the effect and the influence to the image shapes by the operational conditions can be known simultaneously.

The photograph of four pairs of the (N_2-CO) doublet is shown in Fig. 16 obtained by shifting the main magnetic field strength by little and little. The spectral lines inclined depending on their position on the photographic plate and some of lines were wedge-shaped having a construction around the middle portion. Similar effects on the ion beam focusing can be seen on the CRT screen as shown in Fig. 14 by the electric detection with the device mentioned above. The spectral lines of A and C in the figure have the opposite inclinations.

Fig. 16. (N_2-CO) doublet lines taken at the intermediate focus-point on a photographic plate.

Fig. 14 shows the image profile taken when the entering angle of ion beam to the first magnetic analyzer was changed a little on either side by the deflector placed at the exit of the electric field. In addition the image shift is also shown in each case, which was arised by changing the ion beam accelerating voltage by a fractional difference of about two parts in 10^4. The square signal for switching ion beam accelerating voltage is transmitted by a wireless device set from the ground to high voltage level. Peaks upper in each trace have higher energy than lower one. A and C in the figure have opposite inclination but the peaks of higher energy shifted almost parallel to lower ones and energy focusing condition was not
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established. In the traces of B, two shifting lines arised by the energy difference across each other and energy focusing condition seems to be established at its crossing point.

To know the direction focusing condition, a tungsten wire of 0.3 mm diameter was inserted around the middle of the direction defining slit of about 0.8 mm width. Fig. 15 shows the line image profiles of \( \text{C}_2\text{H}_4\text{-C}_2\text{D}_2 \) doublet obtained in this device. The image lines made split by two kinds of ion beam passing through both sides of the wire looks like a split pin and the direction focusing condition seems to be established at the lowest trace. In spite of establishing the focusing condition as shown in Fig. 14 and 15, the resolving power was not so higher than that of other traces.

Such effects were thought to come mainly from the inhomogeneous distributions of the magnetic analyzer field not only in the radial direction but also the azimuthal ones and/or from a slight lack of orthogonal aligning between the electric and the magnetic field strength. And it was also thought, though rather small effects, that there was a slight lack of paralleling of the Herzog shield plates and the boundary faces of the electric field and some disturbance of stray field of the magnet at the boundaries.

The homogeneity of the first magnetic field was carefully checked and remeasured and was raised to within 0.1% along the azimuthal direction which was 0.5% in earlier time. After then realigning both fields was carried out. The first magnetic field was shifted by a few cm outside from its theoretical position, because the inner side in the magnet gap was found to be more homogeneous than the outer.

The final focusing adjustment was then started, which included changing slightly the entrance angles to both fields, shifting the ion collector, paralleling the main and the collector slit to the direction of magnetic field strength and other possible adjustments such as getting best focusing. Fig. 17 shows the peak traces obtained in early stage of the adjustment. The resolving power was greater than that of Fig. 14 in spite of not establishing of the focusing condition. Fig. 18 shows the doublet of \( \text{C}_2\text{H}_4\text{-C}_2\text{D}_2 \) taken during above adjustment work. The fractional mass difference of this doublet is about one part in \( 10^4 \). Fig. 19 shows the \( \text{N}_2\text{-CO} \) doublet taken after above adjustment work. The half height resolution is estimated to be about 800,000 in the case of the lowest trace in Fig. 18.

Fig. 20 shows the same ion peak \( \text{N}_2 \) obtained by changing the electrostatic potential by its fractional difference of \( 2.2 \times 10^{-6} \). From the figure, flat top peaks were seen and it was found the half height resolution of 1,000,000 or somewhat higher was attained. But the image broadening ascribed to the ion beam oscillation affected by some stray oscillation magnetic field was observed.

4. Doublet Mass Difference Measurement
The mass difference of \( \text{N}_2\text{-CO} \) doublet was preliminarily measured with the visual peak matching method at half height resolution
Fig. 18. Doublet peaks of \((\text{C}_2\text{H}_4-\text{C}_2\text{D}_2)\) during precise focus adjustment.

Fig. 19. Doublet peaks of \((\text{N}_2-\text{CO})\).

Fig. 20. Artificial doublet of \(\text{N}_2\) taken by changing the electric potential by its fractional difference of \(2.2 \times 10^{-6}\).

of 300,000–400,000. The voltage divider is the one used in reconstructed Ogata-Matsuda type mass spectroscope and other circuits except for high voltage switching circuit which is wireless device, are also similar ones used in the Ogata-Matsuda type described in elsewhere. As seen in Fig. 21, there existed a large systematic deviation depending upon whether a high or low member of the doublet was observed when the home-made relay coil for switching the electrostatic potential was excited. Such a deviation had previously been observed in the case using the same voltage divider\(^{10}\). The cause of such a systematic error was that the stray magnetic field from the home-made relay coil deflected ion beam slightly. So, this relay coil was replaced by a light-optical device and the square signal for switching the mercury relay coil on the high voltage level in the voltage divider was transmitted by switching light quanta from photodiodes. The result obtained with digital peak matching method which was previously developed successfully with the reconstructed Ogata-Matsuda type mass spectroscope\(^{11,12}\) is shown in Fig. 22. The symbol A and B show the state that the mercury relay coil on the high voltage level is on or off when the higher member of doublet is observed. As
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CO - N₂

Average

Fig. 21. Measured mass differences of (N₂-CO) doublet by visual peak matching.

N₂-CO

Average

Fig. 22. Measured mass differences of (N₂-CO) doublet by digital peak matching.
shown in the figure, the systematic deviation by the stray magnetic field from the relay coil is not found, but the small deviation depending on each run is still remained. The cause of such a deviation may come from the small differences of the focusing condition along the spectral lines as seen in Fig. 14. However such a deviation may be able to be almost cancelled out adopting the average of the measured values because the small deviation of the focusing does not seem to be unidirectional among the runs of measurement.

In the digital peak matching, the mass peaks of the doublet components were accumulated in each 200 channels of the pulse height analyzer used in multiscaler mode in which the peak width was estimated to be about 100 channels. The peaks were digitally printed out as a step-wise function of channel number X, and the channel difference between the representative points X0's of the peaks were calculated by an electric calculator or the counting rate of each channel was transmitted to a computer and the channel difference was printed out by an on-line computer program. The true matching point resistance $\Delta R_0$ of one run was calculated from about 15 sets of $\Delta R$ and the channel difference at that time of $\Delta R$ by linear interpolation. As a representative point, the so-called median, which is the channel number of the half area of the mass peak, was adopted in this case. The details of the method calculating $\Delta R_0$ are found in elsewhere\(^{10, 11}\)

The doublet mass differences were calculated from the relation

$$\Delta M = (1 + \alpha) \frac{\Delta R_0}{R} \cdot M$$

For evaluating the amount of $\alpha$-correction, one hydrogen mass differences of doublets ($C_2H_4-C_2H_2$) and ($C_3H-C_3$) were measured during each series of doublet mass difference measurement. In the measurement of the doublet ($N_2-CO$) $\alpha$ was $5.87 \times 10^{-5}$ which caused rather large correction of $0.66 \mu u$. One of the causes of such deviation is thought to come from the charging up effect on the surfaces of electrodes of the electrostatic analyzer and of the slit blades covered by hydrocarbon film from diffusion pumps and vacuum sealing materials. To reduce the correction factor, the electrodes and the slit blades were puffed by powdered aluminum oxide and cleaned up by ethylether.

After the clean up of the electrodes and the slit blades, the mass differences of ($C_2H_4-C_2D_2$), ($C_2H_4-CND$), ($C_2D_2-CNH_2$) at mass 28 and ($C_2D_2-C_3$) at mass 36 were measured. And during these measurements, the correction factors were $1.5 \times 10^{-4}$, $1.5 \times 10^{-4}$, $4.5 \times 10^{-4}$ and $4.0 \times 10^{-4}$ respectively.

5. Result and Discussion

The doublet mass differences obtained are shown in Fig. 23, 24, 25 and 26 and in Table 2 in which the previous adjusted values obtained from the reconstructed Ogata-Matsuda type mass spectroscope are also included for reference. As seen in the table, all of the present values are consistent with the previous one but deviating to small direction. And so, there is a probability that either or both of them may have small systematic errors. To test the reliability of these doublet mass differences values, it is necessary to remeasure these doublets under the better condition than the present

<table>
<thead>
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<th>Table 2. Measured mass differences.</th>
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<tr>
<td>Present</td>
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<td>$N_2-CO$</td>
</tr>
<tr>
<td>$C_2H_4-C_2D_2$</td>
</tr>
<tr>
<td>$C_2D_2-CNH_2$</td>
</tr>
<tr>
<td>$C_2H_4-CND$</td>
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<tr>
<td>$C_2D_6-C_3$</td>
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<td>(unit: $\mu u$)</td>
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</tbody>
</table>

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\( \text{C}_2\text{H}_4 - \text{C}_2\text{D}_2 \)

Fig. 23. Measured mass differences of (C\(_2\)H\(_4\)-C\(_2\)D\(_2\)).

\( \text{CND} - \text{C}_2\text{H}_4 \)

Fig. 24. Measured mass differences of (C\(_2\)H\(_4\)-CND).
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\[ \text{CNH}_2 - \text{C}_2\text{D}_2 \]

Fig. 25. Measured mass differences of (C\textsubscript{2}D\textsubscript{2}-CNH\textsubscript{2}).

\[ \text{C}_2\text{D}_6 - \text{C}_3 \]

Fig. 26. Measured mass differences of (C\textsubscript{6}D\textsubscript{2}-C\textsubscript{3}).
case, that is, the better homogeneity of the main magnetic field strength over the wide region must be realized and the ion source must be operated with much more stable condition. And in future when the conditions of ion source operation could be stabilized much more, the measuring accuracy of doublet mass differences would be greatly improved.

In the present case, the defocusing along the spectral lines exists as previously mentioned, and even if the good focusing condition is obtained at the beginning of the doublet mass difference measurement, the focus condition will be often disturbed by many factors: for example the change of the ion source condition, charging up effect on the electrodes and the slit blades, etc. If the focus condition has a tendency of shifting to unidirectional side, the doublet mass differences obtained will deviate systematically.

The mass excesses of D, H, N and O were calculated from five doublet mass differences shown in Table 2 by least square treatment. The results obtained are shown in Table 3 and the associated errors also shown on the left side in the table. However as seen in Table 2 the mass excess of D is calculated from only one doublet mass difference (C_2D_6-C_3), and the mass excesses of H, N are calculated from the doublet mass differences of (C_2H_4-C_2D_2), (CNH_2-C_2D_2) and (CND-C_2H_4) and mass of D. So in such a case the errors obtained from the above least square treatment may be estimated to be too small. Because the residual $\nu$ is zero as to (C_2D_6-C_3) and (N_2-CO) doublet values and it is obtained from three doublets (C_2H_4-C_2D_2), (CNH_2-C_2D_2) and (CND-C_2H_4).

In other word, the numbers of the unknowns are four D, H, N, O and the numbers of the kinds of doublets measured involving these unknowns are five. So far calculating the masses of D, H, N and O, they must be too few to use the least square treatment. In order to avoid the possible under-estimation of the errors, the authors adopted the following correction for the quoted errors. The error of D estimated from the associated error of the (C_2D_6-C_3) doublet mass difference is 0.067 $\mu$u and 2.23 times larger than that of the least square calculation. And this error seems to be reasonable and so other errors of H, N, O are multiplied by 2.23 times to that from the least square calculation. These are shown at the right side in Table 3.

The comparison between the present results and others and 1971 mass table values is shown in Fig. 27, 28, 29 and 30 and Table 4. All of the present values are consistent with present authors' previous values. As to the mass of H the agreement among the mass spectroscopic values so far obtained seems to be satisfactory, and Smith's value in 1970, of which the associated error is smallest among the values reported so far, is consistent with the present value. On the other hand, the D mass values seems to be rather largely scattering compared with the case of H and the consistency between the present value and Smith's one is bad. As for the N and O values, the present results seem to be consistent with Smith's ones.

Finally the authors would like to touch on so-called “Table values” of atomic masses.

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**Table 3. Present results of mass excesses of H, D, N and O.**

The left column of errors is obtained from least square treatment. The right column is the errors corrected from the error of (C_2D_6-C_3) doublet.

<table>
<thead>
<tr>
<th>Element</th>
<th>Least Square Error</th>
<th>Corrected Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>7.825.050</td>
<td>014</td>
</tr>
<tr>
<td>D</td>
<td>14.101.912</td>
<td>030</td>
</tr>
<tr>
<td>N</td>
<td>3.074.075</td>
<td>046</td>
</tr>
<tr>
<td>O</td>
<td>-5.085.281</td>
<td>123</td>
</tr>
</tbody>
</table>

(unit: $\mu$u)
Fig. 27. Comparison of the present results of D with others.

Fig. 28. Comparison of the present results of H with others.
Present Status of the Two Stage Double Focusing Mass Spectroscope at Osaka University

Fig. 29. Comparison of the present results of N with others.

Fig. 30. Comparison of the present results of O with others.
Table 4. Comparison of the present results with others.

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>D</th>
<th>N</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brookhaven'58&lt;sup&gt;58&lt;/sup&gt;</td>
<td>7824.958± 87</td>
<td>14101.834±103</td>
<td>3074.314±200</td>
<td>-5086.049±345</td>
</tr>
<tr>
<td>Brookhaven'59&lt;sup&gt;59&lt;/sup&gt;</td>
<td>7825.928±278</td>
<td>14103.348±370</td>
<td>3074.878±515</td>
<td>-5087.046±1140</td>
</tr>
<tr>
<td>Minnesota'56&lt;sup&gt;56&lt;/sup&gt;</td>
<td>14102.118±556&lt;sup&gt;56&lt;/sup&gt;</td>
<td>3073.487±270&lt;sup&gt;56&lt;/sup&gt;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Minnesota'57&lt;sup&gt;57&lt;/sup&gt;</td>
<td>7824.663±200</td>
<td></td>
<td></td>
<td>-5085.850±533</td>
</tr>
<tr>
<td>Minnesota'66&lt;sup&gt;66&lt;/sup&gt;</td>
<td>7825.220±30</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Minnesota'67&lt;sup&gt;67&lt;/sup&gt;</td>
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<td></td>
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<tr>
<td>Argonne'67&lt;sup&gt;67&lt;/sup&gt;</td>
<td>7825.010±28</td>
<td>14101.887±27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Argonne'69&lt;sup&gt;69&lt;/sup&gt;</td>
<td>7825.055±40</td>
<td>14101.760±200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Osaka (GE.ED.)'68&lt;sup&gt;68&lt;/sup&gt;</td>
<td>7824.990±140</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Osaka (GE.ED.)'69&lt;sup&gt;69&lt;/sup&gt;</td>
<td>7825.005±49</td>
<td>14101.933±57</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Princeton'70&lt;sup&gt;70&lt;/sup&gt;</td>
<td>7825.029±5</td>
<td>14101.771±10</td>
<td>3073.937±14</td>
<td>-5085.567±26</td>
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<tr>
<td>Osaka'72&lt;sup&gt;72&lt;/sup&gt;</td>
<td>7825.065±30</td>
<td>14101.930±40</td>
<td>3073.910±140</td>
<td>-5085.750±250</td>
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<tr>
<td>Princeton'75&lt;sup&gt;75&lt;/sup&gt;</td>
<td>3074.001±11</td>
<td>-5085.384±22</td>
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<td></td>
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<tr>
<td>Mass Table'71&lt;sup&gt;71&lt;/sup&gt;</td>
<td>7825.220±40</td>
<td>14101.220±70</td>
<td>3074.400±130</td>
<td>-5084.980±200</td>
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<tr>
<td>Mass Table'71&lt;sup&gt;71&lt;/sup&gt; (recal.)</td>
<td>7825.050±10</td>
<td>14101.820±20</td>
<td>3074.020±30</td>
<td>-5085.480±60</td>
</tr>
<tr>
<td>Present</td>
<td>7825.050±35</td>
<td>14101.912±67</td>
<td>3074.075±115</td>
<td>-5085.281±307</td>
</tr>
</tbody>
</table>

As seen in the figures, the table values are deviated unidirectionally to heavy side against almost all mass spectroscopic values. Such a discrepancy is seen in 1964 mass table<sup>6</sup>. And so, the latest mass table values, even in the important mass substandards, may be in error. However, the consistency of the recalculated values involving Smith’s values as an input datum was improved greatly<sup>13</sup>

Under such present status in the precise atomic mass field, the discrepancies between the mass values so far obtained must be thoroughly and critically investigated. In such investigations, the systematic error ones are the most important still at present.

References
2) H. Nakabushi, I. Katakuse and K. Ogata, OULNS 70-1, p. 9; OULNS 72-1, p. 48.
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