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NATIONAL BUREAU OF STANDARDS REPORT

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A NEW MASS SPECTROMETER

by

Robert M. Mills

and

Charles C. Pugh



U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

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U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

A NEW MASS SPECTROMETER

ABSTRACT

This paper describes a time-of-flight mass spectrometer being developed which will be used in investigations of combustion processes. The instrument is rather unique in that its operation is similar to the phase focusing in a linear accelerator; a defocusing effect is used rather than a focusing one. The advantages of a time-of-flight spectrometer as well as the advantages of the particular type being developed are discussed. After the necessary equations are derived, a description of the apparatus so far assembled is given.

1. Introduction

At the present time, many researchers are exploring the basic mechanisms of flames. The question as to the nature of the role played by the charged particles found in a flame arises in their investigations, but, as yet, no explanation has been commonly accepted. Three experimental approaches to this problem have been microwave absorption, probe measurements, and mass spectrometry. Of these three, the last enjoys the greatest popularity because of the high sensitivity obtainable with mass spectrometers. Foner and Hudson (1) and Eltenton (2) have designed an apparatus which ionizes flame gases for mass spectrometer analysis. Knewstubb and Sugden (3), as well as Deckers and van Tiggelen (4) have made a more straightforward approach, sampling the ions to be analyzed directly from the flame. It is planned to use this sampling technique at the National Bureau of Standards.

It is proposed to construct a flame-analyzing mass spectrometer, which will supplement the theoretical work being done here on flame mechanisms. The results will be used to check whether insufficient vacuum conditions inside the instruments of previous researchers caused misleading recombinations of the ions. Eventually, it is hoped to use the instrument to investigate the presence of negative ions in a flame, a subject pertinent to the current theoretical work being done at NBS, but, as yet, largely unexplored.

After preliminary investigations concerning the construction of a mass spectrometer, it is planned to build a time-of-flight (T.O.F.) instrument. The basic principle of such an instrument is that heavy ions take a longer time to reach the end of a drift tube than do light ions of equal energy. A time-of-flight instrument has the advantage over a magnetic mass spectrometer of relatively low cost and simplicity of construction. The limitations on the accuracy of a T.O.F. instrument are placed on the construction of the electronic equipment rather than on the mechanical alignment of the instrument. Absolute calibration is easier in T.O.F. instruments since the three parameters involved, tube length frequency, and magnitude of applied voltage, are easily measured and controlled. On the other hand, hysteresis, saturation, and fringe effects make calibration of magnetic mass spectrometers more difficult unless a permanent magnet is used. If the magnetic spectrometer does use a permanent magnet, the only variable parameter is the acceleration voltage, and care must be taken so that the ionic current which is transmitted through the instrument is not changed as the voltage is swept.¹ Furthermore, d-c amplifiers are usually used with magnetic spectrometers in order to amplify the steady stream of ions which are collected, whereas T.O.F. instruments can use tuned a-c amplifiers which distinguish between ion current and background noise. The major disadvantage of a T.O.F. instrument is its low resolving power when confronted with ions of high mass. However, since it is thought that almost all of the ions in a flame are light (of mass less than 100), a T.O.F. machine seems likely to be useful.

2. Theoretical Discussion of Apparatus

The design of the time-of-flight instrument which is to be constructed is somewhat different from the T.O.F. mass spectrometers presently in existence. Essentially, it involves a modified linear accelerator. Others have pointed out the usefulness of accelerators as mass spectrometers (5,6). A linear accelerator, in its simplest form, consists of a line of coaxial metal tubes, alternate tubes being connected electrically to each side of a radio frequency source. The length of the tubes, the frequency and the amplitude of the rf voltage are adjusted so that an ion emerges from the field free tubes into a gap at the proper time in order to acquire an acceleration.

¹ This change could result from electrostatic focussing effects on the ions or from the ion collisions with the walls of the drift tube before they are collected.

The scheduling of the positions of the ion is not designed, as one might expect, so that the ions are ejected into a gap at the peak voltage. Instead, the ion emerges into the gaps at the times indicated by the asterisks in Figure 1. Note that going from one gap to the next is equivalent to a phase shift of 180° .² Thus, the two waves are drawn, and alternate waves are used for alternate gaps. One can see that this scheduling of the arrival of the ions results in a bunching effect. A heavy ion which travels a bit slow arrives at the next gap late. However, it is more strongly accelerated due to the large electric field in the gap, which enables it to catch up. Likewise, lighter ions experience a smaller acceleration since they arrive at the gap early. The magnitude of this bunching effect depends on the slope of the rf voltage at the time the ion is in the gap. In fact, the effect may change to a spreading effect if the ions arrive in the gap during the negative portion of the slope (i.e., fast ions arrive at the end of the tube early and are made to go even faster). This latter effect is desirable since it produces the separation of the ions according to their masses. It is desirable to have the spreading effect occur during the largest possible portion of the cycle, which suggests the use of a saw-tooth (S.T.) rf voltage. The effect of going from one gap to the next is now as shown in Figure 2. If the slope of the saw-tooth voltage is positive at the first gap, it must be negative at the second gap.

The voltage at the second gap must have a negative slope to obtain the spreading effect. Thus, a positive sloped saw-tooth rf voltage is applied to the entrance of the tube as shown in Figure 3. If the length of the drift tube and the voltage used to give the ions their initial acceleration are such that an ion of a particular mass remains in the drift tube for a whole number of complete cycles, one can see, by referring to Figure 2, that unlike other masses, this particular mass has neither gained nor lost energy after it has gone through both gaps. If an ion remains in the drift tube less than 360° , the ion gains energy, but if it stays slightly more than 360° it loses energy. The fact that one particular mass neither gains nor loses energy is true regardless of the portion of the cycle through which the ion passes at the first gap, assuming zero flyback time for the saw-tooth wave. Thus, the instrument is able to collect a steady stream of ions instead of the pulses

² Since the polarity of the second drift tube gap relative to the first has been reversed, the voltage at the second gap is the same as that found at the first, multiplied by -1.

which the usual T.O.F. instrument requires, and makes it possible to collect a larger effective current, thereby improving sensitivity. However, the advantage of being able to use an a-c amplifier is retained as will be explained in the section describing the collector system. A further advantage of the design over the usual T.O.F. instruments is that there is no need for a gate or pulse voltage, which is of the same high radio frequency.

In order to write down the equations describing the performance of the proposed spectrometer, the following definitions are used:

- V - the total voltage through which an ion has fallen.
- V_{d-c} - the d-c acceleration voltage through which an ion passes before it emerges into the first saw-tooth gap.
- V_{st} - the peak to peak saw-tooth rf voltage applied at each end of the drift tube.³
- t - the time in seconds required for the ion to pass through the drift tube.
- T - the period of the rf applied voltage.
- L - the length of the drift tube in meters.
- v - velocity of the ion travelling through the drift tube.
- e - charge of an electron = 1.66×10^{-19} coulombs.
- m - the mass of the ion (in kilograms, unless otherwise stated)
- n - the number of rf cycles the ion remains in the drift tube.
- amu - Atomic mass units

³ The wave form of the saw-tooth wave is actually similar to that shown by the broken line in Figure 2. However, the slope of the wave rather than its actual maximum value is of importance. Thus V_{st} is defined as the maximum voltage difference occurring in the wave represented by the solid line.

Now:

$$(1) \quad t = \frac{L}{v}$$

but since

$$\frac{1}{2} mv^2 = eV$$

$$v = \sqrt{\frac{2eV}{m}}$$

Using this in (1) and realizing that $t = nT$

$$(2) \quad t = \frac{L \sqrt{m}}{\sqrt{2eV}} \quad \text{or}$$

$$(2a) \quad \frac{T \sqrt{V}}{\sqrt{m}} = \frac{L}{n \sqrt{2e}}$$

V in equation (2) is the total voltage through which an ion has fallen after it has entered the drift tube but before it passes into the last gap. An ion which has an atomic mass larger or smaller than the ion which stays in the drift tube exactly 360° will arrive at the second saw-tooth gap ahead or behind the 360° ion by an amount given by:

$$(3) \quad \frac{dt}{dm} = \frac{L}{2 \sqrt{2eVm}}$$

which can be simplified by using (2) to read

$$(3a) \quad \frac{dt}{dm} = \frac{t}{2m}$$

Since the $1.66 \times 10^{-27} \frac{\text{kg}}{\text{amu}}$ conversion factor cancels out, the m in (3a) can be expressed directly in amu.

Now, if (3a) is multiplied by the rate of change of the saw-tooth voltage at the second gap, an expression is obtained giving the difference in potential through which an ion falls at the second gap for a unit change in mass number.

If perfect linearity and zero flyback time are assumed, the rate of change of the S.T. voltage is given by $\frac{V_{st}}{T}$.

$$\text{Thus} \quad \frac{dV}{dm} = \left(\frac{t}{2m} \right) \left(\frac{V_{st}}{T} \right) \quad \text{or}$$

$$(4) \quad \frac{dV}{dm} = \frac{n}{2m} V_{st}$$

Since it has already been concluded that the total effect on a 360° ion after going through both S.T. gaps is to neither gain nor lose energy, the dV is equal to the voltage received by an ion which is heavier or lighter than a 360° ion after it has gone through the two S.T. gaps.

There is another effect which causes a variation in the net potential of an ion and which, so far, has been neglected. The potential of the ions in the drift tube varies with time because of the saw-tooth voltage applied at the first gap. Equation (2a) indicates that t will also vary (i.e., ions will not always remain in the tube for exactly 360°) unless T is made to change with V by frequency modulation. However, the use of frequency modulation adds to the complexity of the instrument, especially since T does not vary linearly with V . The variation of t will be small if V is large. This may be calculated from the change in total potential of an ion due to the saw-tooth voltage variation.

First, though, it will be helpful to find the change in t due to the S.T. voltage.

$$\frac{dt}{dV} = - \frac{L m^{\frac{1}{2}}}{2 \sqrt{2eV^3}}$$

Using (3)

$$(5) \quad \frac{dt}{dV} / \frac{dt}{dm} = - \frac{m}{V}$$

An ion of atomic mass number m and ions of atomic mass numbers $m \pm 1$ all have a variation in final V due to the S.T. voltage. Therefore, resolution of ions differing by one mass number requires that the absolute value of the variation be not more than one half of dV/dm .

$$(5a) \quad \left| \frac{V_{st}}{T} \cdot \frac{dt}{dV} \cdot \frac{V_{st}}{2} \right| < \left| \frac{V_{st}}{T} \cdot \frac{1}{2} \cdot \frac{dt}{dm} \right| \quad \text{or}$$

$$\left| \left(\frac{dt}{dV} / \frac{dt}{dm} \right) V_{st} \right| < 1$$

Which gives

$$(5b) \quad \left| -m \frac{V_{st}}{V} \right| < 1.$$

In the above analysis, the fluctuation in the potential of ions in the drift tube is given by dV . Again, m in (5b) is expressed directly in atomic mass numbers.

There might be a second variation in the final energy of the ions which would further limit the resolution of the instrument. The initial thermal energies of ions are usually neglected in mass spectrometer work because, at room temperature, the average thermal energy amounts to only 0.04 ev. (7) However, there is some question about this at the elevated temperatures of flames. If the thermal energy appears as an initial velocity, the final energy of the ions is a function of the direction of the thermal velocity. It was decided to determine the range in the thermal velocities of the ions selected by our apparatus by experiment.

If n is to equal one, equation (4) indicates that the resolution becomes small for increasing mass numbers. But, equation (2b) shows that n can be increased as m is increased, without changing the values of T , V , or L . This has two advantages. Besides improving the resolution of high masses, it reduces the required frequency ranges of the radio frequency saw-tooth generator. It is planned to vary n as follows:

| <u>Mass Region</u> | <u>n</u> |
|--------------------|----------|
| 1 to 10 | 1 |
| 10 to 17 | 3 |
| 17 to 26 | 4 |
| 26 to 37 | 5 |
| 37 to 50 | 6 |
| 50 to 65 | 7 |
| 65 to 82 | 8 |
| 82 to 101 | 9 |

2. Harmonic Masses and Modifications Needed for Their Elimination

Suppose L , V and T are chosen so that $n=s$ satisfies equation (2b) for the particular mass which is to be measured. Any other mass which satisfies (2b) by making n an integer and which is not equal to s will pass through the two S.T. gaps without gaining or losing energy. These unwanted masses are called harmonic masses. The situation is similar to the case of a car traveling at 20 mph being able to pass through a series of traffic lights which are set for 40 mph. If n is equal to one, only heavier harmonics can exist. Lighter harmonics exist if n is greater than 1.

Elimination of the harmonic masses may be attained by using two more drift tubes as shown in Figure 4. One additional tube would be sufficient except for the fact that an even number of gaps are needed in order that the saw-tooth voltages at the gaps cancel out. The length of the middle tube is not important since it cannot be used to analyze the masses. This can be explained as follows. An ion which has fallen through an accelerating voltage can arrive at the end of a drift tube early for two reasons. It can be of lighter mass and thus travel faster, or it could have started earlier. Thus, one needs to schedule the ions so that they arrive at the end of the drift tube at a known time. This could be done by pulsing the ion beam and, thus, allowing the ions to start in bunches. Or scheduling could be done with a saw-tooth voltage as planned. However, the sawtooth voltages have cancelled one another after the ion passes into the middle tube and hence they are not scheduled. Thus, the middle tube will be made short. It was convenient to make it Δ° long. The length of the first drift tube will be such that ions remain in the tube for a time equivalent to just under a multiple of 360° of the rf voltage and the length of the last drift tube will be such that ions remain in the tube for some integral number of complete cycles.



That this arrangement does not allow harmonics to pass, is shown by the following pertinent equations. The following symbols are defined:

- n_1 - nearest number of whole cycles an ion stays in the first drift tube.
- n_2 - nearest number of whole cycles an ion stays in the last drift tube.
- n_{H_1} - nearest number of whole cycles a harmonic ion could stay in the first drift tube.
- n_{H_2} - nearest number of whole cycles a harmonic ion could stay in the last drift tube.
- Δ - number of degrees less than $n_1 360^\circ$ which an ion spends in the first drift tube.

All of the above numbers are defined to be positive.

The time, in degrees, an ion takes to pass through the first tube is $n_1 360^\circ - \Delta$ (e.g., point A in Figure 2). An ion of another mass which is a harmonic (i.e., receives the same net energy from the saw-tooth voltages applied at the ends of the first drift tube) spends $n_{H_1} 360^\circ - \Delta$ degrees (point B) in the tube. If this same mass is to be a harmonic in the last drift tube, the ratio of the times of the non-harmonic and harmonic masses in the last drift tube must be the same as the ratio of the times in the first drift tube:

$$(6) \quad \frac{n_1 360^\circ - \Delta}{n_{H_1} 360^\circ - \Delta} = \frac{n_2 360^\circ}{n_{H_2} 360^\circ}$$

In the discussion that follows, n_1 will be made equal to $n_2 = n$.

Harmonic masses may be found by considering n_{H_1} to be the independent variable in equation (6) and n_{H_2} to be the dependent variable, using the appropriate values of n as discussed earlier.⁴ Strictly speaking, a mass can be considered to be a harmonic of both tubes only if n_{H_2} is a whole number. But it must be known how close to a whole number n_{H_2} can be and still have the corresponding mass considered to be a harmonic by instrument. Which of the masses to be considered harmonics were determined by the following criteria:

The average particle has a thermal energy fluctuation of $\pm \frac{1}{2} KT = \pm 0.0604 \text{ ev}$ at flame temperature. It is probably safe, then, to assume that the instrument will be able to distinguish ions which have energy differences of .5 ev or more. If V_{st} is to equal 30 volts (so that (5b) holds up to $m = 100$), the corresponding difference in arrival time is 6 degrees. This requires that:

$$\left(n_{H_2} \quad 360 \right) - \left(n_{H_2}' \quad 360 \right) > 6^\circ$$

$$(6a) \quad \left| n_{H_2} - n_{H_2}' \right| > 0.0167$$

Since n_{H_2} was defined to be a whole number, n_{H_2}' was used to denote the value of the dependent variable in (6) which might not be a whole number.

⁴ Since masses above 100 will not be considered, the following program was used to look for harmonics:

| Mass in this Range | | Values of n_{H_1} to be investigated. In case number is not a whole number, next lower number is used. |
|--------------------|----------------------------|----------------------------------------------------------------------------------------------------------|
| $n=1$ | 1 to 10 | 2 to 10 |
| 3 | 10 to 17 | 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 |
| 4 | 17 to 26 | 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17 |
| : | : | : |
| n | (n^2+1) to $(n+1)^2 + 1$ | 1, 2, ..., (n-1), (n+1), ..., $n/\sqrt{n^2+1}$ |
| : | : | : |
| 9 | 82 to 100 | 1, 2, ..., 8. |

A suitable value of Δ has not yet been established. It should be small since the first Δ degrees of the saw-tooth voltage cycle cannot be used. This can be seen by referring to Figure 2.

Ions of the correct mass starting through the first drift tube during the first Δ degrees receive a relatively large net loss in energy after passing into the middle drift tube; the rest of the ions (i.e., correct ions leaving after the first Δ) gain a small amount of energy. Thus, since the instrument is made to accept only the small energy gain, ions entering the first tube during the first Δ are discriminated against by the instrument and are not collected. However, this does not reduce the sensitivity as much as might be expected, since ions starting at this time are lost anyway due to the fact that S.T. oscillators cannot be made to have zero return time and perfect linearity at the beginning and end of the cycle.

To find how small Δ can be and still have the instrument distinguish harmonics, it is required that there be at least a difference of 6° between the time-of-flight in the last tube of an ion which is a harmonic in the first tube and time-of-flight of another mass which could be a harmonic in the last tube:

$$(6b) \quad \left| \frac{n_{H_1} \times 360^\circ - \Delta}{n \times 360^\circ - \Delta} n \times 360^\circ - n_{H_2} \times 360^\circ \right| > 6^\circ$$

The first term on the left represents the time taken in the last tube by a mass which was a harmonic in the first tube; the second term corresponds to the time taken by a possible harmonic in the last drift tube. It was determined that the absolute value of $n_{H_2} - n_{H_1}'$ is the smallest when the values of n and n_{H_1} in equation (6) are themselves small. Thus, when $n = 1$ and $n_{H_1} = 2$ in (6b) and Δ is chosen to equal 7° , this value of Δ in (6a) gives the minimum value of $n_{H_2}' - n_{H_2}$ equal to 0.0198 and this was taken to be an acceptable guard against harmonics, at least until proven by experiment.

The ions which have been discussed above represent masses which are able to pass as harmonics through both the first and last drift tubes. There is a second type of harmonic mass for the instrument as a whole which does not pass through either one of the tubes as such. Instead, the mass is able to gain and then lose (or vice versa) enough energy to be collected with the wanted ions. This could possibly occur if the ion

starts during the first Δ degrees. But the value of the mass which is able to do this is not independent of the starting time, resulting in an additional ion current which will be the same for all instrument settings. An ion could pass as the second type of harmonic if the first tube is Δ degrees less than 360° and the last is Δ degrees longer than 360° , since the same amount is gained in the first drift tube that is later lost in the last. One would not be able to distinguish between different values of n . By making the first drift tube 7° less than 360° and the last just equal to 360° , there is an increase of about 0.5 electron volts per unit increase of n in the final energy of the ions to be collected.

Using more than one drift tube to get rid of the harmonic masses also improves the resolution of the instrument. Equations may be derived corresponding to (4) when three drift tubes are used. From (2a) and (3a):

$$(7) \quad \frac{dt}{dV} = \frac{1}{2} \frac{t}{V}$$

$$(7a) \quad \frac{dt}{dm} = \frac{1}{2} \frac{t}{m}$$

Assuming that V_{d-c} is large enough so that, effectively, there is no variation in the final energy of the ion from the saw-tooth voltage (i.e., that equation (5b) holds), then:

$$(7b) \quad \left(\frac{dV}{dm} \right)_2 = - \frac{V_{st}}{T} \left[\frac{dt}{dV} \left(\frac{dV}{dm} \right)_1 + \frac{dt}{dm} \right]^5$$

The first term in brackets is due to the change in energy imparted to the ion by the first tube. The second term, as with the single drift tube case, is due to the slowness of a heavy ion or to the extra speed of a light ion in reaching the end of the last tube. $\frac{dt}{dV}$ is negative; $\frac{dV}{dm}$ is negative because

of the negative slope at the end of the first drift tube. The first term, then, is positive. The term $\frac{V_{st}}{T}$ is negative

because the voltage decreases with time at the end of the last tube.

⁵ Subscripts refer to the number of tubes used to separate the ions

Using (7), (7a), and (4):

$$\left(\frac{dV}{dm}\right)_2 = -\frac{V_{st}}{T} \left[\left(\frac{1}{2} \frac{t}{V}\right) \left(\frac{nV_{st}}{2m}\right) + \frac{1}{2} \frac{t}{m} \right]$$

or, since $t = nT$:

$$(7c) \quad -\left(\frac{dV}{dm}\right)_2 = \frac{n^2}{4m} \frac{V_{st}^2}{V} + \frac{n}{2} \frac{V_{st}}{m}$$

Equation (7c) gives only the change in energy of the ions resulting at end of last drift tube. But there has already been a change at the end of the first tube, and this change, equation (4), should be added to (7c). Thus:

$$(7d) \quad -\left(\frac{dV}{dm}\right)_2 = \frac{n^2}{4m} \frac{V_{st}^2}{V} + \frac{n}{m} V_{st}$$

It is planned to make $V_{st} = 30$ volts and V about 3,000 volts. Also, if reference is made to the discussion of the values of n to be used with the various masses, it is found that $\frac{n^2}{m} < 1$. Thus, the first term is small. But, the remaining term makes (7d) twice as large as the resolution for the single drift tube case. Equation (7d) has replaced only (4). Equation (5b) is still valid for the 3 drift-tube instrument. Equation (2b) is valid if L is taken to be the length of each drift tube and n is the number of degrees spent in this particular tube divided by 360° .

3. Design of Apparatus

The values of the terms in equation (2a) will be as follows:

| | |
|-----------------|------------------------------------------|
| V_{st} | - 30 volts peak to peak |
| V_{d-c} | - 3000 volts |
| L_1, L_2, L_3 | - 55.1, 1.1, 56.2 cm |
| n | - increase with m as discussed earlier |
| $\frac{1}{T}$ | - from 0.45131 to 1.35319 Mc/sec |

The change in the length of the second and third drift tubes needed to compensate for the energy change at the end of the first tube is found from equation (2a).

$$(8) \quad \frac{dL}{dV} = \frac{1}{2} \frac{nT \sqrt{2e}}{\sqrt{mV}} = \frac{1}{2} \frac{L}{V}$$

This amounts to 0.0037 mm/volt for the second tube and 0.0955 mm/volt for the third. The largest value of $\frac{dL}{dV}$ is $7^\circ \times 9$ (i.e., when $n = 9$), which corresponds to:

$$\frac{63^\circ}{360^\circ} 30 \text{ volts} \approx 5 \text{ volts}$$

Thus the second and third drift tubes should be increased, at most, by 0.02 mm and 0.5 mm, respectively. These corrections were neglected in computing L_2 and L_3 .

The collector system must be able to distinguish between masses by their energies. If the final energy of the ion to be measured is E electron volts, it is planned to apply a potential barrier in front of the collector which is first equal to $E + \epsilon$, then is changed to $E - \epsilon$. The value of ϵ is such that the resulting change in collector current is due entirely to the on-off switching of the mass to be measured.

Figure 5 is a sketch of the electrical connections. The connections were made so that the velocity of the ions stays high until just before they enter the Faraday cage. A retarding field, which is needed for a secondary electron repeller, could not be applied at the entrance of the Faraday cage because the velocity of the ion has already been reduced by the potential barrier. Therefore, a long slender Faraday cage was built and depended on to prevent secondary electrons from escaping. An electronic lens is used to ensure that the ions travel to the back end of the cage before colliding with the walls. The cut-off control is adjusted until the ionic current is cut off when the α and S.T. generators are not operating. The cut-off control is also used to select different values of n . The 3000 volt d-c supply is regulated and has a fine voltage control. The 110 volt supply consists of dry cell batteries which are also used with the vacuum indicating ionization gauge.

Figure 6 shows the burner, the flame chamber assembly, and the intermediate vacuum chamber. The burner consists of two concentric brass tubes. The outside diameter of the larger tube is $3/4$ of an inch. The inner tube feeds gas to the end of burner where it mixes with oxygen and burns. A ring which fits loosely around the burner compresses a teflon ring against the burner and flame chamber body to form a vacuum seal. An observation window on the top side of the assembly makes it possible to check on flame size and shape. The assembly is cooled by a water jacket which surrounds the vacuum chamber where the flame burns. Pressures below one mm of Hg can be obtained by using Cenco Rotovac Pump when the flame is not burning. Pressures of 2 to 7 cm are obtained with the flame burning. A closed end mercury monometer is used to determine the flame chamber pressure. The flame chamber is connected to the pump through a water trap and a four liter flask both of which are used as ballasts. Glass wool is stuffed into both tubes of the burner to stabilize the flame at low pressure.

Throughout the design of the entire instrument, special efforts were made to permit its easy disassembly for alterations or cleaning. For this reason, bolts were used to connect the intermediate vacuum section with the burner section. A lead foil gasket aids in making a vacuum seal. A compressed "O" ring makes a vacuum seal against the glass "T", which forms the intermediate region proper. An oil diffusion pump which has a pumping speed of about 25 liters/sec at 10^{-3} mm

is connected to the bottom of the glass "T" with a short piece of rubber hose. The hose fits firmly over the butt joint formed by the ends of the diffusion pump and "T", and then is covered with several coats of shellac. Two vacuum gauges, a thermocouple and an ionization gauge (not shown in figures), are sealed directly to the glass "T". The first orifice is made by drilling a hole six thousandths of an inch in diameter through .004 in. platinum foil. Platinum was used to withstand the heat from the flame and so that the hole would not cause the foil to rip when atmospheric pressure is applied. The foil is sandwiched between a ring and the burner assembly. By placing the ring on the burner side, the first orifice can be aligned with the second orifice before the rest of the burner assembly is bolted in place. The ring is held in place with six screws which allow easy replacement of the foil. The second orifice is 0.010 in. diam. It is similar in design except that it is located on the end of a tube which extends the length of the intermediate region as shown in the figure. This allows the distance between orifices to be small without impairing the pumping speed of the diffusion pump. It is desirable to have the orifices close together to minimize ion-air collisions and to facilitate the passage of the ions through both orifices. More will be said about this later. A tight vacuum seal is made at the intermediate-drift tube region junction with hard black sealing wax.

A second mechanical vacuum pump is on order which is similar to the one being used as a roughing pump for the diffusion pumps. The new pump will permit reducing the pressure in the flame chamber still further and thereby lowering the pressure in the rest of the apparatus. This increase in pumping capacity will be necessary if the equipment is modified to work with flames at atmospheric pressure at some future time.

The electrical equipment needed for the vacuum gauges and the controls for the diffusion pumps has been constructed and tested. The design of this equipment follows fairly closely the suggestions of the manufacturer.

Ion currents as large as 10^{-7} amps have been measured coming through the first orifice, but further construction of equipment is necessary before measurements can be made on the current passing through the second orifice and reaching the collector. It has been shown, however, that because of ionic losses, the ion current can be a function of the accelerating

voltage which means that the masses to be measured should not be swept by changing the voltage. The shape of the electric field in the intermediate vacuum region where the ions receive their first acceleration causes electrostatic focusing of the ions. The focal length of this lens will be controlled by the potentiometer shown in Figure 5.

Figure 7 shows the drift tube and collector assembly. The diffusion pump connection and another set of vacuum gauges are not shown. The diffusion pump used has three stages and is capable of reducing the pressure in the drift tube region to below 10^{-5} mm of Hg with the flame burning. The drift tubes themselves are cut from copper tubing and have copper end plates soldered at each end to center the tubes. The plates are square to offer a minimum of impedance to the pumping speed. They are bolted together with nonconducting nylon screws. Sandwiched between the plates are teflon insulating washers and fine tungsten screens which have an ion absorption of about 1 per cent. The screens are stretched across the ends of the tubes to accurately define the electric fields in the gaps. Standard tapered glass joints are used to connect the diffusion pump and the end glass piece to the long glass tube which surrounds the drift tubes. Rubber bands hold both joints together. A spring is compressed between the drift tube assembly and Faraday cage to prevent vibrations. The Faraday cage and drift tube assembly are kept from separating by a constriction in collector end of the drift tube and two 0.032 in. diam tungsten wires at the other end. Electrical connections are made internally with teflon covered wire and brought out at the collector end of the apparatus through 6 electrical vacuum seals.

Three pieces of electronic equipment remain to be constructed. The current detection instrument should be able to go down to 10^{-15} amps. Since the ion beam is modulated by the generator, an a-c amplifier can be used; its design will probably be similar to that used in the amplifying part of a vibrating reed electrometer. The generator frequency will be tuned to the a-c amplifier and will be a relatively low value (i.e., 30 cps). Its peak to peak voltage should not be any larger than twice the energy separation of masses corresponding to nearly the same T, but different n's (i.e., one volt). The frequency of the saw-tooth generator must be variable from 1.35 to 0.450 Mc/sec in steps as small as 6 kc/sec. It must be as linear as possible between \angle and 360° , but there are no linearity requirements during the rest of the cycle. Its peak to peak voltage needs to be somewhat above 30 volts.

4. Future Improvements

There are several possibilities for increasing the resolution of the mass spectrometer. The most obvious way is to add more drift tubes as was done to eliminate harmonics. This can be done by increasing the length of the entire instrument, by increasing the frequency of the saw-tooth wave or by decreasing V_{d-c} . However one must compensate for phase changes along the instrument if its length is comparable with the wavelength of light at frequency of the S.T. generator. Also, equation (5b) limits the amount by which V_{d-c} can be decreased. Overcoming this limitation is the second possibility of increasing the resolution.

The change in voltage per atomic mass difference for an instrument having $(2r-1)$ drift tubes can be shown to be:

$$\left(\frac{dV}{dm}\right)_r = -\frac{V_{st}}{T} \left[\frac{dt}{dV} \times \left(\frac{dV}{dm}\right)_{r-1} + \frac{dt}{dm} \right] + \left(\frac{dV}{dm}\right)_{r-1}.$$

Using equations (7) and (7a),

$$\left(\frac{dV}{dm}\right)_r = -\frac{V_{st}}{T} \left[\frac{1}{2} \frac{t}{V} \left(\frac{dV}{dm}\right)_{r-1} + \frac{1}{2} \frac{t}{m} \right] + \left(\frac{dV}{dm}\right)_{r-1}.$$

$$(9) \cdot \left(\frac{dV}{dm}\right)_r = -\frac{nV_{st}}{2} \left[\frac{1}{V} \left(\frac{dV}{dm}\right)_{r-1} + \frac{1}{m} \right] + \left(\frac{dV}{dm}\right)_{r-1}.$$

As an example, consider the case of $r = 3$:

$$(9a) \left(\frac{dV}{dm}\right)_3 = \frac{n^3 V_{st}^3}{8m V^2} + \frac{3 n^2 V_{st}^2}{4 m V} + \frac{3 n V_{st}}{2 m}.$$

The first two terms are small enough to be neglected because of the relative sizes of V_{st} and V_{d-c} ($\approx V$). Therefore, if it were possible to overcome the limitation of (5b), V could be reduced to make the addition of more stages practical without changing T or the overall length of the instrument. Also, if V_{st} can be increased and/or V decreased, the first terms in (9a) could become significant and the resolution increased greatly. This is equally true for other values of r . There is another limitation on how small V_{d-c} can be made which will be discussed in the appendix, but the magnitude of V_{st} is limited only by the engineering problems in the design of the S.T. generator, if it were not for equation (5b).

A second type of bunching has been considered, which has been used in other types of T.O.F. mass spectrometers (8) and which will allow an increase in the magnitude of V_{st} . It is a somewhat academic idea so far, since it has not been possible to apply it to an instrument having more than one drift tube.

Consider the case of a single tube. Equation (5b) can be interpreted to require that the relative positions of the ions in the drift tube should not change to a significant degree since this would upset their schedule. If the magnitude of V_{st} , is too large, ions starting early would not have as large a velocity as those starting later, which results in a continuous change of the relative positions of the ions. However, this can be allowed if the ion schedule has been changed in a particular way. A positive sloped sawtooth wave can be applied to the gap through which the ions pass before entering the drift tube. Ions which start early should pass through this gap when the S.T. voltage is low, while ions leaving later should be accelerated more by the larger value of the S. T. wave. Somewhere in the drift tube, then, it may be possible for the faster ions to catch the slower ones. In other words, at one point along the drift tube, the ions may be bunched. After the ions pass this point, the fast ones will have overtaken and passed the slower ones, so that there will be only one spot, for any given mass, at which the ions are bunched. However, ions starting at different points in the cycle have different energies as they pass through the drift tube. The collector system planned should distinguish between different masses by their energy. This idea cannot be employed unless the variation in energy of a particular mass which is imparted to it at the first sawtooth gap can be cancelled out. This could be done by requiring that the ionic bunchings take place exactly at the center of the tube. By the time the ions reached the far end of the drift tube, the fast ions would be ahead of the slow ones by the same amount that the fast ones were behind the slow ions at the starting end of the drift tube. If another positive sloped wave is used at the far end of the drift tube, the variation in energy received at the first S.T gap would be cancelled out. The point at which the ions bunch is a function of the mass; thus this system does not pass harmonic masses (since the ions bunch only once). Thus, this system differentiates between ions of different masses. If the ions are too heavy, they bunch at a point further down the drift

tube and have not spread out as much by the time they reach the far end of the tube. No ion of this heavier mass reaches the end of the drift tube in time to receive the voltage needed in order to cancel out that which it received at the first S.T. gap. The opposite is true of ions which are too light.

Derivation of new equations requires the definition of τ , as the time at which an ion enters the drift tube. The symbol ℓ = the point at which the ions bunch in the drift tube. In the proposed system, $\ell = L/2$. Let t' be the time an ion takes to reach point ℓ if it passed the first S.T. gap when the voltage is zero. Then, requiring that all ions of a certain cycle arrive at ℓ at the same time means that:

$$t' - \tau = \frac{\ell}{v} = \frac{\ell \sqrt{m}}{\sqrt{2e} \left(V_{d-c} + \frac{V_{st}}{T} \tau \right)}$$

or

$$\frac{V_{d-c} + \frac{V_{st}}{T} \tau}{m} = \frac{\ell^2}{2et'^2} \left(\frac{1}{1 - \frac{\tau}{t'}} \right)^2$$

This can be expanded:

$$\frac{V_{d-c} + \frac{V_{st}}{T} \tau}{m} = \frac{\ell^2}{2et'^2} \left(1 + 2 \frac{\tau}{t'} + 3 \left(\frac{\tau}{t'} \right)^2 + 4 \left(\frac{\tau}{t'} \right)^3 + \dots \right)$$

If $\frac{\tau}{t}$ is small:

$$(10) \quad \frac{V_{d-c} + \frac{V_{st} \tau}{T}}{m} = \frac{l^2}{2et^{1/2}} \left(1 + 2 \frac{\tau}{t} \right)$$

In order for (6) to hold for all values of τ , it is required that:

$$(10a) \quad \frac{V_{d-c}}{m} = \frac{l^2}{2et^{1/2}}$$

and

$$(10b) \quad \frac{V_{st}}{m} = \frac{l^2 T}{et^{3/2}}$$

In effect, this results in discarding the condition that required equation (5b) to hold in introducing the effect to eliminate harmonics. A thorough investigation of the resolution expected of this type of system has not been made or of the values of the voltages and frequency which would be required. But as for the latter, it is probable that a higher V_{st} and lower V_{d-c} would be required.

5. Summary

The characteristics of the mass spectrometer which has been described are summarized as follows:

By using the saw-tooth wave scheduling, it is possible to utilize a large per cent of the ionic beam emerging from the first orifice instead of pulses of ions. The value of the mass which is being collected is known if the frequency of the saw-tooth wave being used and the other parameters of the instrument are known. Neighboring masses are separated by at least 2.7 electron volts on the energy scale (for mass 100). This resolution is achieved by the "light ions travel faster" property; equation (5b) makes the "light ions are made to travel even faster" effect small. Harmonic masses are separated from the mass to be collected by at least 0.5 electron volt.

It is not known whether this 0.5 ev separation is large enough. The deciding factors are how monoenergetic the initial ionic beam is and the quantum mechanical probability of an ion passing through a 0.5 electron volt barrier. The range of energies of the ions is determined by their thermal velocities together with the direction of these velocities and by any kinetic energy variation which the ions receive as they pass from a high to low pressure region. The former has been shown to be much less than 0.5 volts. And the transmission of ions through a 0.5 volt barrier 2 centimeters thick was calculated to be negligibly small(9).

It should be noted that (5b) is a limitation only on the larger masses. A 3 kilovolt supply is being used because it was readily obtainable. If it becomes necessary, V_{d-c} can be increased or the limitations of (5b) can be overcome by the bunching effect described earlier or possibly by frequency modulation. By increasing the value of V_{st} , both the resolution and the harmonic separation should be improved.

APPENDIX

The problem here dealt with is how much acceleration voltage between orifice A and B is needed in order that the average ion leaving A reaches the end of the drift tube without colliding with the plate of orifice B or with the walls of the drift tube.

ϕ = the voltage at orifice B when orifice A is grounded.

ϕ is negative.

x is the distance from plate A, measured toward B.

Voltage = $V(x) = \frac{\phi x}{b}$ where b is the distance between orifice A and orifice B (in meters).

$$- \nabla V(x) = \text{field} = - \frac{\phi}{b}$$

\bar{a} = acceleration = $\frac{\text{field} \times \text{charge}}{\text{mass}}$ and assuming charge = e

$\bar{a} = - \frac{\phi e}{bm}$, a constant. In a field of uniform acceleration

$$\bar{x} = \frac{1}{2} \bar{a} t^2 \quad \text{and} \quad \bar{v} = \bar{a} t.$$

Thus, the time necessary for a particle with zero initial velocity in the longitudinal direction to get from A to B is

$$t = \frac{2b}{\bar{a}} = b \sqrt{\frac{2m}{-\phi e}}$$

$$\text{The longitudinal velocity at B} = v = at = \sqrt{\frac{-2\phi e}{m}}$$

The average particle:

1. Starts at the center of orifice A
2. Has a radial energy of $\frac{1}{2}KT$ ($=\frac{1}{2}mv^2$) due to the heat of the flame from which it is emitted.

$$KT = mv^2 \text{ or } v = \sqrt{\frac{KT}{m}}$$

where T = flame temperature $\approx 1400^\circ K$

The radial displacement of the average particle is

$$b \sqrt{\frac{2m}{-e} \frac{KT}{m}} = b \sqrt{\frac{2KT}{-e}} = b \sqrt{.173/-e}$$

Thus:

$$/e/ = \frac{.173b^2}{(r.\text{displ.})^2}$$

The average particle can travel any radial distance less than the radius of orifice B and still get through. The problem is (a) what voltage is required between the two orifices such that the average ion has radial displacement equal to r_B (the radius of orifice B)? In the instrument being constructed, $b = 8.5\text{mm}$ and $r_B = .127\text{mm}$. Thus, $/e/ = 774$ volts. (b) when the average ion has fallen through 774 volts and has barely missed the lip of orifice B, will it get to the end of the drift tubes without colliding with the tubes' walls?

The critical inside dimensions of the system are as follows:

The longitudinal distance from orifice B to :

1. point C (in Figure 6) 1 $\frac{25}{32}$ in.
2. point D (in Figure 6) 4 $\frac{3}{8}$ in.
3. point E (in Figure 7) 48 in.

The radial distance from the center of orifice B to:

1. point C 3/32 in.
2. point D 7/16 in.
3. point E 9/16 in.

Since $\frac{48}{9/16} > \frac{4+3/8}{7/16} > \frac{1+25/32}{3/32}$, and since both longitudinal and radial velocities are essentially constant, it is only necessary to consider ions hitting the exit lip of the drift tube. That is, if an ion's radial displacement is less than 9/16 in. during the time necessary for it to get to the end of the drift tube, it will not collide with any part of the inside of the tube. The time that it takes a particle to go E-B distance is:

$$(E-B) \frac{-2\phi e}{m}.$$

Since the radial velocity is $\sqrt{\frac{KT}{m}}$, the radial displacement at the end of travel from B to E equals

$$(E-B) \times \sqrt{\frac{m}{-2\phi e}} \frac{KT}{m} = (E-B) \sqrt{\frac{KT}{-2\phi e}} = .0108 \text{ meters} \quad 9/16 \text{ in.} =$$

.0143 meters.

Thus an average particle getting through orifice B at 774 volts also gets through the drift tube.

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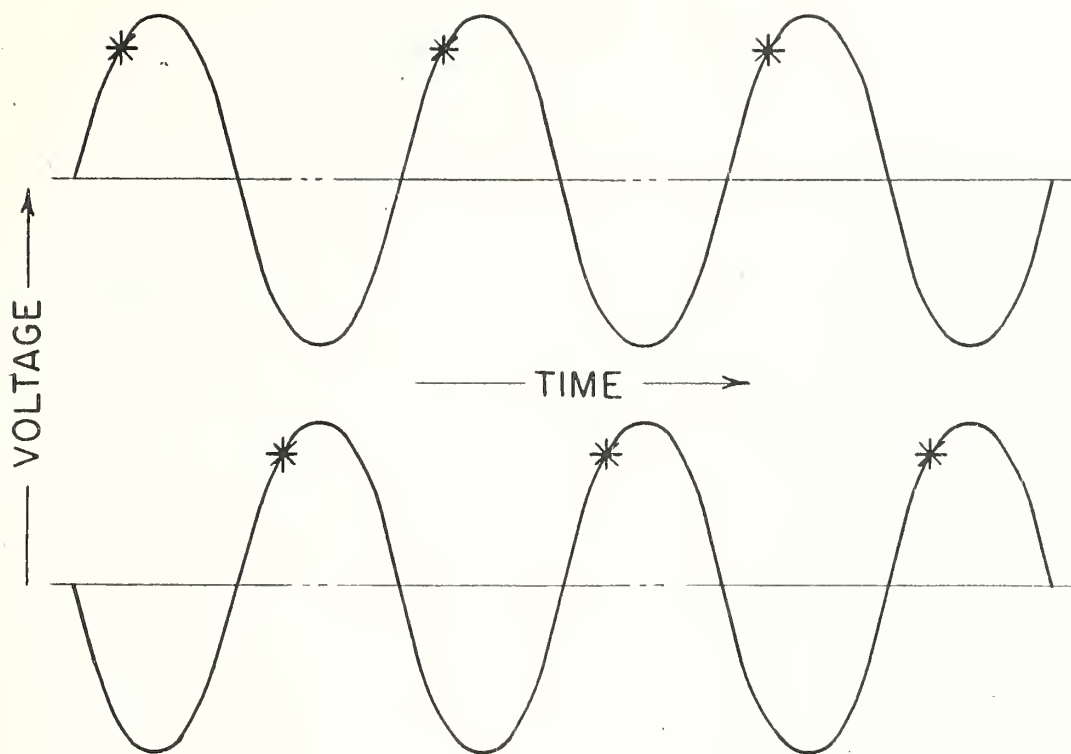


FIG. 1

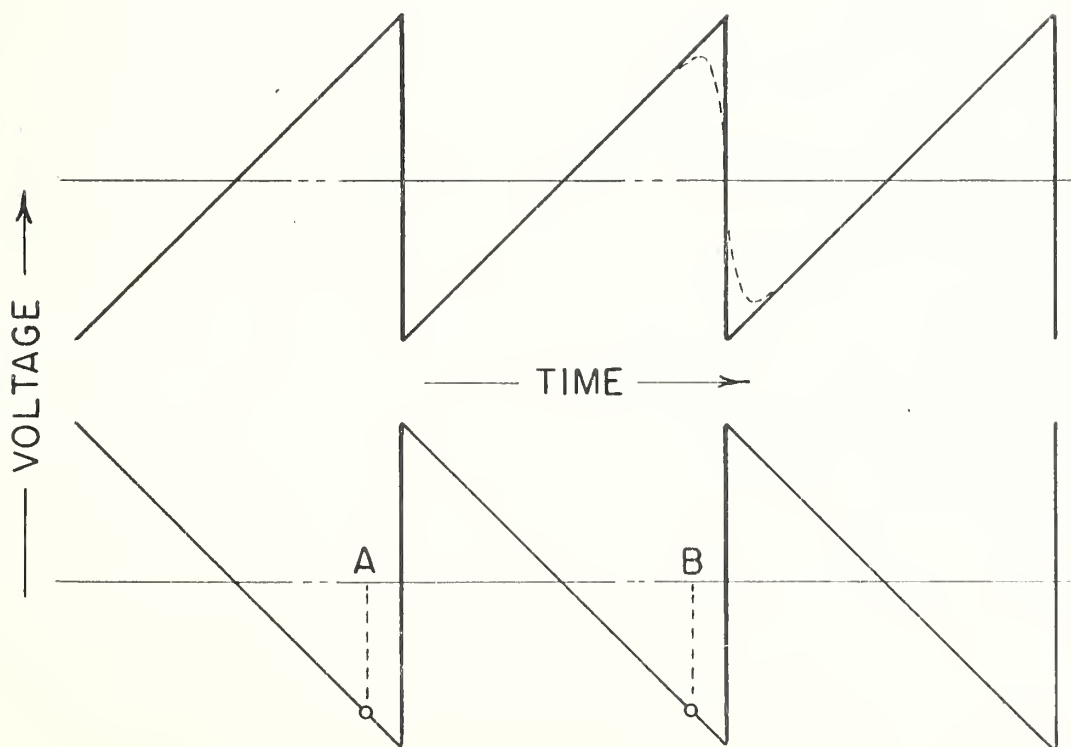


FIG. 2

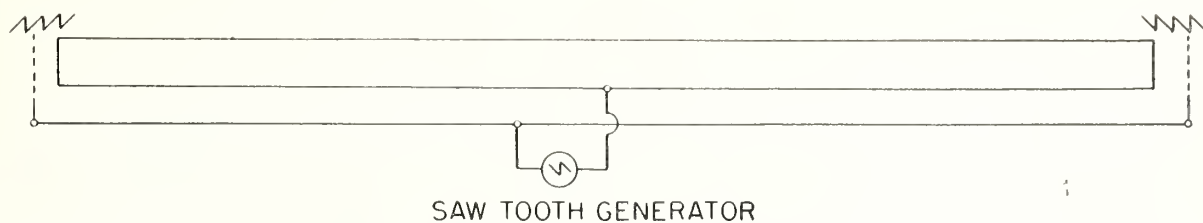


FIG. 3

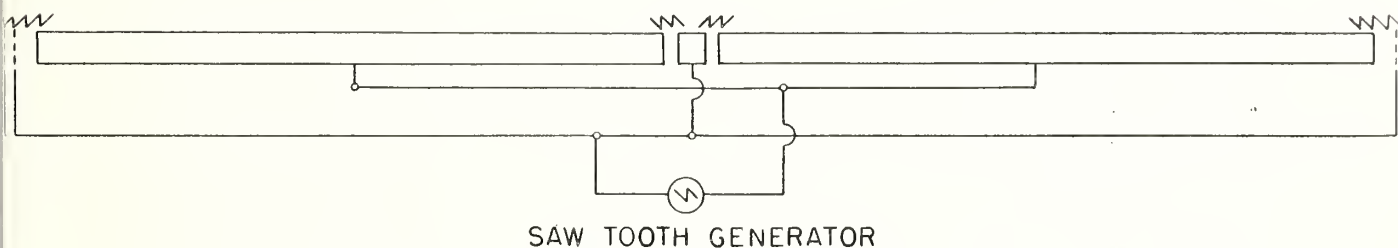


FIG. 4

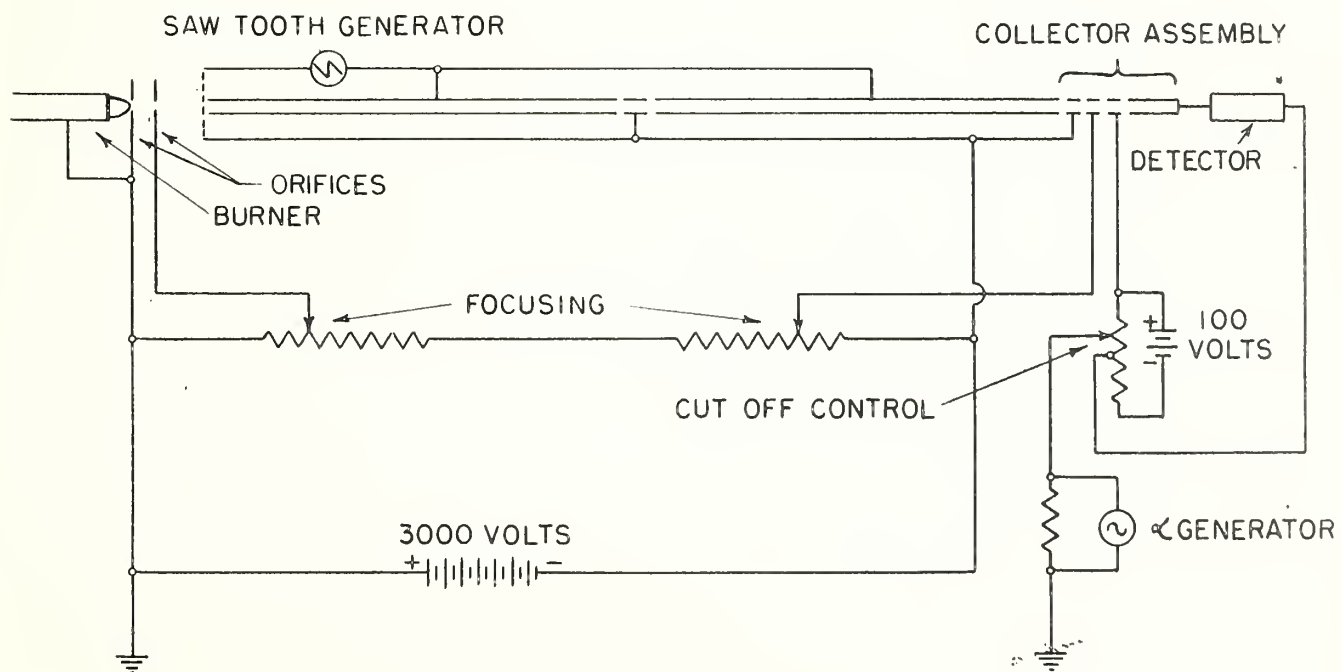


FIG. 5

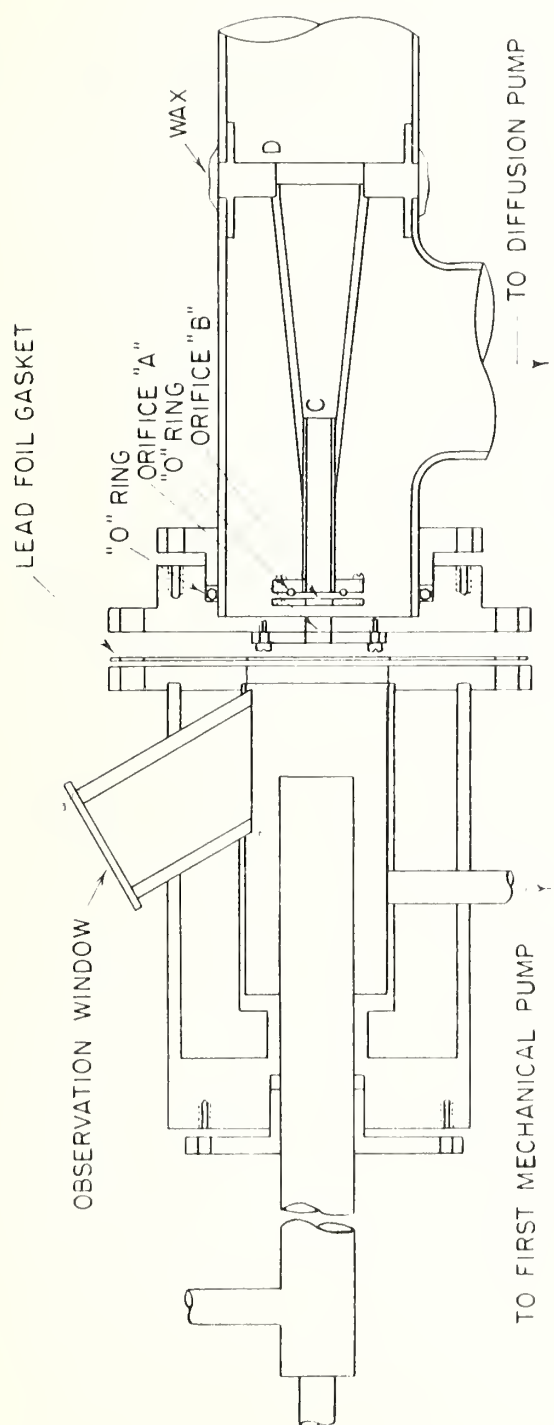
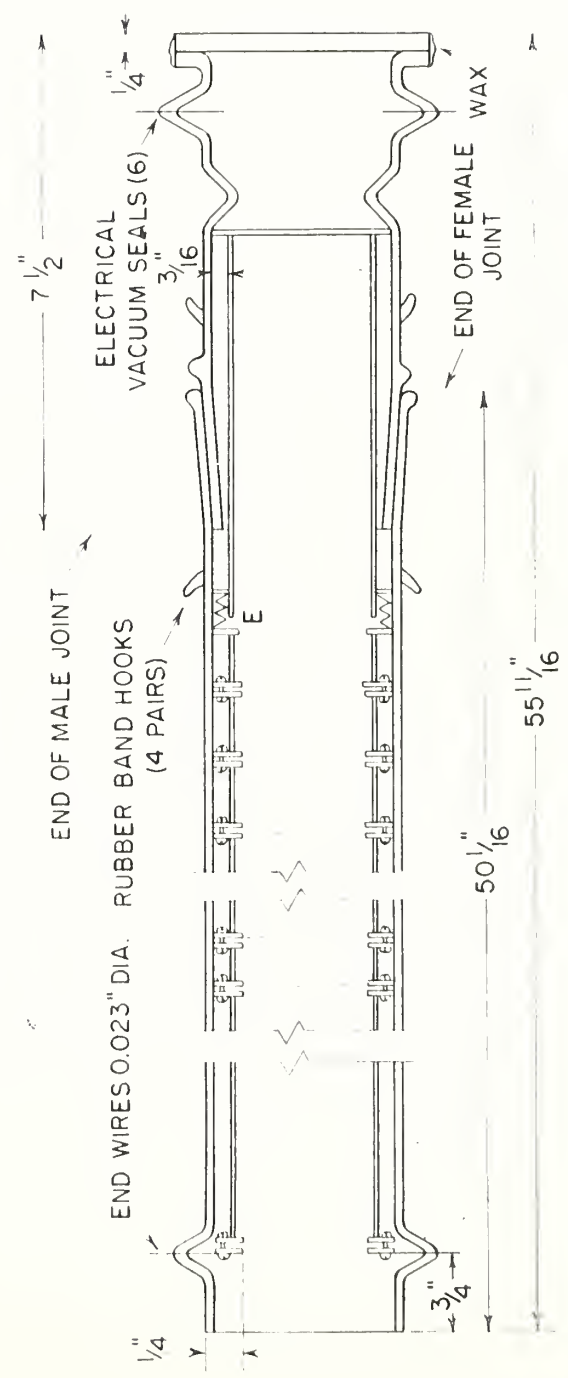


FIG. 6 - BURNER AND INTERMEDIATE SECTIONS OF MASS ANALYZER



FRONT VIEW OF DRIFT TUBE
END PLATE IN POSITION

FIG. 7 - DRIFT TUBE AND COLLECTOR SECTIONS

U.S. DEPARTMENT OF COMMERCE

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