Time-of-Flight Mass Spectrometer with Improved Resolution

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A new type of ion gun is described which greatly improves the resolution of a nonmagnetic time-of-flight mass spectrometer. The focusing action of this gun is discussed and analyzed mathematically. The validity of the analysis and the practicability of the gun are demonstrated by the spectra obtained. The spectrometer is capable of measuring the relative abundance of adjacent masses well beyond 100 amu.

INTRODUCTION

THIS paper describes the improved mass resolution made possible by a new ion gun in a nonmagnetic, time-of-flight (TOF) mass spectrometer. Although the properties of this gun may make it useful for focusing electrically accelerated ion beams in other applications, the discussion will be restricted to mass spectrometers which have been tested.

Following a brief description of TOF spectrometers, their resolution is discussed. The new ion gun is then described and its focusing action is analyzed mathematically. Experimental results substantiating the general theoretical conclusions are presented. Finally, a method is described for measuring relative mass intensities with the increased precision possible in this type of instrument.

GENERAL DESCRIPTION

The most straightforward TOF spectrometers consist of an ion source and a collector situated at opposite ends of an evacuated tube. We shall consider only this type and, for additional information, refer the reader to the comprehensive bibliography on mass spectrometers compiled by Dibeler.[1] The performance of such instruments has been reported by Cameron and Eggers,[2] by Wolff and Stephens,[3] and by Katzenstein and Friedland.[4] The ions are formed in the ionization region of the source, usually by electron bombardment. They are then accelerated out of the source toward the collector by either one or a series of constant electric fields. In some cases the fields are applied continuously. In others the accelerating fields are pulsed on at the end of ion formation. If the accelerating pulse lasts until all ions have left the source, all ions receive essentially the same energy. If, with a single constant accelerating field, the pulse cuts off before any of the ions leave the source, all ions receive essentially the same momentum. In either case the velocity of the ions in the free flight path is a function of the ratio of their charge, q, to their mass, m. Therefore, when the ions reach the collector they have separated into bunches corresponding to q/m. If only singly charged ions are present, the lightest group reaches the detector first and is followed by groups of successively heavier mass. Thus, each source pulse results in a mass spectrum which can easily be displayed by connecting the ion collector to the vertical plates of an oscilloscope. An expanded portion of such a spectrum (obtained with the improved ion gun) is shown in Fig. 1.

The known abundances of the xenon isotopes displayed are 128, 2%; 129, 26.4%; 130, 4.1%; 131, 21.2%; 132, 26.9%; 134, 10.4%; 136, 8.9%.

ADVANTAGES AND DISADVANTAGES

The detailed design of a TOF mass spectrometer depends on its applications. However, these applications need not be discussed to show the values of the new ion gun and the performance it makes possible. These values can be made clear if one summarizes the three main advantages and the chief disadvantage of TOF spectrometers.

A unique advantage is the speed with which a spectrum can be obtained conveniently. With practical parameter values a complete spectrum can be obtained every few microseconds. Thus, one can study how the relative intensities of different ions vary when source conditions change rapidly. For example, one could find appearance potentials and identify radicals quickly by measuring the spectrum as a function of the easily controllable energy of the ion-producing electron beam. For this application, not only the speed of response but also the existence of a field free source region during ionization is important.

A second feature of the TOF spectrometer is that the entire mass spectrum can be recorded for each accelerating pulse. Thus, it is possible to measure relative intensities accurately even though source conditions might vary unpredictably, provided only that the variations affect each mass in the same way. In contrast, rather elaborate controls are required in most other types of mass spectrometers to prevent source changes. When the TOF spectrometer is used to determine a mass ratio precisely, the ratio is measured for each accelerating pulse, as described below.

The third major advantage of the TOF spectrometer is that its accuracy depends on electronic circuits

[1] V. H. Dibeler, Anal. Chem. 26, 58 (1954).
[2] A. E. Cameron and D. F. Eggers, Jr., Rev. Sci. Instr. 19, 605 (1948).
[3] M. M. Wolff and W. E. Stephens, Rev. Sci. Instr. 24, 616 (1953).
[4] H. S. Katzenstein and S. S. Friedland, Rev. Sci. Instr. 26, 324 (1955).

rather than on extremely accurate mechanical alignment and on the production of highly uniform, stable magnetic fields. The freedom from stringent geometric conditions simplifies construction. Dispensing with the critical magnetic field removes size and shape restrictions which otherwise might keep the evacuated chamber so small as to be sensitive to stray electric fields produced by dirty or corroded inner surfaces.

Since the ion formation process itself has a rather low duty cycle, commonly on the order of 0.1 to 10%, it would seem that the ion currents should be much lower in intensity than those obtained with a conventional deflection type mass spectrometer. There are, however, two factors which tend to increase the magnitude of the ion signals, so that the amount of information concerning the mass spectrum which can be obtained per unit time can be as large or larger than that obtained in a conventional instrument.

The first of these is concerned with the fact that a conventional instrument, whether it is operated in the normal manner with a recorder or is operated with a fast scanning system and an oscilloscope display, ordinarily detects only one mass peak at a time. The ion beams of other masses impinge on the vacuum walls and are lost. In contrast, the time-of-flight spectrometer with an oscilloscope display records all the mass peaks which were originally formed by the source and loses only those stray ions which emerge from the source at an angle which causes them to miss the ion detector. For instance, a conventional mass spectrometer scanning from mass one to mass 100 in ten microseconds can display mass peaks which contain ions formed only during an average time of 0.1 microseconds for each peak. A time-of-flight mass spectrometer, displaying a complete spectrum within 10 microseconds, can produce peaks each of which contains ions formed over a period of one microsecond, since few of the ions will be lost from the ionization region in that time. Of course, if only one mass peak is of interest or if a deflection instrument is fitted with photographic plates or multiple ion detectors, these statements do not apply.

The second factor which must be considered is the absence of narrow slits in the ion source and ion detector of a time-of-flight mass spectrometer. This allows one dimension of the ion beam to be much larger than is possible in a conventional instrument, which, in turn, allows a more effective utilization of any given electron beam in producing useful ions.

The main disadvantge of nonmagnetic TOF spectrometers has been their limited resolution. Although such instruments are not designed to give the precise mass measurements possible with the more complex, slower, lower intensity magnetic TOF spectrometers,[5] they must separate adjacent mass units sufficiently well to permit accurate relative intensity measurements. Using a single field source Wolff and Stephens,[3] according to their preliminary report, had completely separated adjacent masses only up to about 20 amu. Katzenstein and Friedland,[4] using a multiple field source, obtained satisfactory resolution to approximately 75 amu, although adjacent masses appear to overlap at this value. With the new ion source, adjacent mass units well beyond 100 amu are completely separated and useful resolution can be obtained to at least 300 amu.

FIG. 1. Oscillogram of the mass spectrum of some xenon isotopes; left to right masses 128, 129, 130, 131, 132, 134, and 136 amu. The peak width is 0.017 μsec.

RESOLUTION OF TOF SPECTROMETER

If all ions were formed in a plane parallel to the source electrodes and with zero initial velocity the flight time would be the same for all ions which had the same q/m, and the resolution would be limited only by the detecting equipment. In practice, the resolving power of a TOF spectrometer depends on its ability to reduce the time spread caused by the ever-present initial space and initial kinetic energy distributions.

A convenient measure of resolution is the largest mass, M, for which adjacent masses are essentially completely separated, i.e., that mass for which the time spread for ions of the same mass just equals the time between adjacent masses. Such a criterion is desirable when abundance measurements are considered proportional to the area of mass peaks. If peak heights are used instead, the mass for which there is no interference between adjacent mass peaks is approximately twice that giving no interference between adjacent peak areas. However, the measurements of peak heights are much more sensitive to variations in the peak shape. Therefore in the remainder of this report the more stringent condition of essentially complete separation of adjacent masses is used.

The ability of the spectrometer to resolve masses despite the initial space distribution is called space resolution, while its reduction of the time spread introduced by the initial kinetic energy distribution is called energy resolution. The initial space distribution can be considered as a deviation of initial position (measured from the exit of the ionization region) about its average, s_0, so that $s_{\max}=s_0+\frac{1}{2}\Delta s$ and $s_{\min}=s_0-\frac{1}{2}\Delta s$. The space resolution problem is to reduce the time spread, $\Delta T_{\Delta s}$. This can be done either by making Δs small compared with s_0, or by space focusing which gives each ion a velocity dependent on s (as well as on q/m) in such a way as to minimize $\Delta T_{\Delta s}$.

[5] Hays, Richards, and Goudsmit, Phys. Rev. 84, 824 (1951).

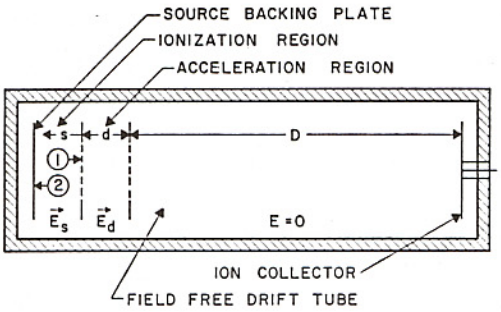

FIG. 2. Basic geometry of the TOF mass spectrometer utilizing the new ion source.

The maximum time spread introduced by initial velocities, ΔT_θ, is the difference in flight times between a pair of identical ions formed at the same s position with the same maximum initial speed, but with oppositely directed velocities. The value of ΔT_θ can be reduced by increasing the ratio of the ion's total energy to its initial energy, or by employing either of two types of energy focusing. One type of focusing involves adjusting the parameters available in the new type of electron gun. The other form of focusing introduces a time lag between the creation of the ions and their acceleration. During this time lag, some of the ions move to new source positions which have the proper flight times to correct for the initial velocity.

Space resolution and energy resolution place opposite requirements on several system parameters. Therefore the best over-all resolution is a compromise between space and energy resolution. The development of the new ion gun[6] by one of us in 1950 permits a more advantageous compromise which yields improved resolution.

IMPROVED ION SOURCE

Description and Comparison with Single Field Source

The new ion source contains two accelerating regions as shown in Fig. 2. While the ions are being formed, the source backing plate voltage is the same as that of the first grid. At all times the second accelerating region, d, has an electric field, E_d, and the region D is field free. Ions are accelerated out of the source toward the collector when a positive pulse is applied to the source backing plate to produce the electric field, E_s. This pulse lasts until all ions have left the first field region.

The double-field source introduces two new parameters, d, and E_d/E_s, which are not available in the single-field source. This increased flexibility makes the double-field source easier to adjust, gives it higher resolution, and makes it much easier to operate because only a fraction of the total voltage is pulsed. The development which follows includes the single-field source as a special case (when d and E_d are zero). However, as is shown by the analysis, the single-field system does not represent a desirable choice of the system parameters.

[6] W. C. Wiley, U. S. Patent 2 685 035.

Flight Time

In moving through the source, any ion with initial energy, U_0, will increase its energy to a value, U, which is independent of m, but dependent on U_0, s, and q,

$$U=U_0+qsE_s+qdE_d. \tag{1}$$

Under these conditions, the time-of-flight can easily be shown to be

$$T(U_0,s)=T_s+T_d+T_D, \tag{2}$$

where

$$T_s=1.02\frac{(2m)^{\frac{1}{2}}}{qE_s}[(U_0+qsE_s)^{\frac{1}{2}}\pm(U_0)^{\frac{1}{2}}], \tag{2a}$$

$$T_d=1.02\frac{(2m)^{\frac{1}{2}}}{qE_d}[U^{\frac{1}{2}}-(U_0+qsE_s)^{\frac{1}{2}}], \tag{2b}$$

and

$$T_D=1.02(2m)^{\frac{1}{2}}D/2U^{\frac{1}{2}}. \tag{2c}$$

The + and − signs in T_s correspond to initial velocities directed respectively away from and toward the collector. The units are given together with typical values in Table I.

In the nonmagnetic TOF spectrometers previously reported, T was approximated by T_D. This is not a valid approximation as it is apparent from Eqs. (2a, b, c) that most of the time spread resulting from variations in initial energy occurs in the source. As an example, for the values of Table I, T_s changes approximately $0.0026m^{\frac{1}{2}}$ μsec for initial energies from 0 to 0.09 ev. For the same range T_D changes only $0.00002m^{\frac{1}{2}}$ μsec.

In the analysis which follows it is convenient to investigate T when $U_0=0$ and $s=s_0$. If we define

$$U_t=qs_0E_s+qdE_d, \tag{3a}$$

and

$$k_0=(s_0E_s+dE_d)/s_0E_s \tag{3b}$$

then $T(0,s_0)$, from a substitution of Eqs. (3) into Eq. (2) becomes

$$T(0,s_0)=1.02\left(\frac{m}{2U_t}\right)^{\frac{1}{2}}\left(2k_0^{\frac{1}{2}}s_0+\frac{2k_0^{\frac{1}{2}}}{k_0^{\frac{1}{2}}+1}d+D\right). \tag{4}$$

Space Resolution

Space focusing depends on the fact that an ion initially closer to the detector (and thus of smaller s value) acquires less energy and is therefore eventually overtaken by ions which have larger initial s values. To find the position at which ions whose initial s values were $s=s_0\pm\frac{1}{2}\delta s$ pass each other, we set $(dT/ds)_{0,s_0}=0$, using Eq. (2) for T and, by substitution from Eq. (3), obtain

$$D=2s_0k_0^{\frac{1}{2}}\left(1-\frac{1}{k_0+k_0^{\frac{1}{2}}}\frac{d}{s_0}\right). \tag{5}$$

This focus condition is the same for all ions and is independent of the total energy of the system. If s_0, d, and D are fixed, E_d/E_s is uniquely determined by Eq. (5), since k_0 can have only one physically significant value. Thus in the double-field system the space focus is obtained by a simple adjustment of E_d/E_s. In contrast, the focus condition for the single-field system ($d=0$, $k_0=1$) is the purely geometric condition, $D=2s_0$.

The focus condition, $(dT/ds)_{0,s_0}=0$, indicates that $T(0,s)$ has either a maximum, minimum, or point of inflection at $s=s_0$. The point of inflection occurs when $(d^2T/ds^2)_{0,s_0}=0$ which requires in addition to the focus condition, that

$$\frac{d}{s_0}=\left(\frac{k_0-3}{k_0}\right)\frac{D}{2s_0}. \tag{6}$$

If d/s_0 is larger than this value, $T(0,s_0)$ is a minimum point; if d/s_0 is smaller, then $T(0,s_0)$ is a maximum point. If $k_0\leqq 3$, then $T(0,s_0)$ is always a minimum point so that for the single-field source ($d=0$, $k_0=1$), the point $T(0,s_0)$ is a minimum. However, for the parameter values usually chosen for best resolution with double-field operation, $T(0,s_0)$ is a maximum.

By utilizing the series expansion of $T(0,s)$ about s_0, we may show that $\Delta T_{\Delta s}$, the change in flight time corresponding to a small change Δs in s about s_0, is given by

$$\Delta T_{\Delta s}=\sum_{n=1}^{\infty}\frac{1}{n!}\left(\frac{d^nT}{ds^n}(0,s)\right)_{s_0}(\Delta s)^n. \tag{7}$$

The measure of space resolution, M_s, is the maximum value of m for which $\Delta T_{\Delta s}\leqq T_{m+1}-T_m$. The time separation of adjacent masses is obtained from Eq. (2) or (4),

$$T_{m+1}-T_m=\left[\left(1+\frac{1}{m}\right)^{\frac{1}{2}}-1\right]T_m\approx\frac{T_m}{2m}. \tag{8}$$

The first term (i.e., $n=1$) in Eq. (7) is made zero by the focusing condition in Eq. (5). If $T(0,s_0)$ is either a maximum or minimum point, $\Delta T_{\Delta s}$ can be evaluated from Eq. (7) with Δs replaced by the maximum deviation of s from s_0, $\Delta s/2$. The successive terms are complicated but can be simplified by the use of approximations without introducing appreciable error. Only the first nonzero term of the series will be used. If $k_0\gg 1$ and $k_0\gg d/s_0$ Eqs. (4), (7), and (8) give

$$M_s\approx 16k_0(s_0/\Delta s)^2. \tag{9}$$

For the parameter values of Table I, $k_0=25$ and $\Delta s/s_0=1$, so that $M_s=400$ amu. Equation (9) shows that space resolution can be made adequate if s_0 is somewhat larger than Δs. This is dependent on D being large since D/s_0 determines k_0 from Eq. (5). Increasing d (as this increases k_0) improves space resolution. Further as d/s_0 becomes large (approaching k_0) the value of M_s is considerably larger than that given by Eq. (9).

TABLE I. Units and typical parameter values for new TOF spectrometer.

Distance (cm)	Electric-field (volts/cm)	q(electronic charge) Energies (ev)	Mass (amu) time (μsec)
$D=40$		$U_t=1600$	$T(0,s_0)=0.76\ m^{\frac{1}{2}}$
$d=1.2$	$E_s=320$	$qs_0E_s=64$	$T_s=0.035\ m^{\frac{1}{2}}$
$s_0=0.2$	$E_d=1280$	$qdE_d=1536$	$T_d=0.035\ m^{\frac{1}{2}}$
$\Delta s=0.2$		$U_0=0.09$	$T_D=0.69\ m^{\frac{1}{2}}$

Energy Resolution

The double-field system brings the ions to their maximum energies in about 5% of the flight time compared with 50% in the focused single-field source. Thus, the disturbing effect of U_0 is reduced because U_0 is a smaller percentage, on the average, of the energy which determines the velocity at each point. To investigate the effects of initial velocities, it is convenient to consider two ions formed at the same initial position s, with equal, but oppositely directed speeds as shown in Fig. 2. Ion 2 moves away from the collector, decelerating due to E_s until it stops. It is then accelerated, returning to s with its original speed. Subsequently, its motion is identical with that of ion 1 which it continues to lag by the "turn-around" time. The time spread, ΔT_θ, introduced by the initial energies is the "turn-around" time (i.e., twice the deceleration time) of an ion having the maximum initial energy being considered,

$$\Delta T_\theta=1.02\frac{2v_0m}{qE_s}=1.02\frac{2(2mU_0)^{\frac{1}{2}}}{qE_s}. \tag{10}$$

If we consider only the effects of initial energy, the maximum resolvable mass, M_θ, is that for which the energy time spread, ΔT_θ, equals the time between adjacent mass peaks, $T/2m$ (i.e., $M_\theta=T/2\Delta T_\theta$). This is evaluated by substituting from Eqs. (4) and (10). If D/s_0 from the focus condition, Eq. (5) is substituted in the result, M_θ is given by

$$M_\theta=\tfrac{1}{4}\left(\frac{U_t}{U_0}\right)^{\frac{1}{2}}\left(\frac{k_0+1}{k_0^{\frac{1}{2}}}-\frac{k_0^{\frac{1}{2}}-1}{k_0+k_0^{\frac{1}{2}}}\frac{d}{s_0}\right). \tag{11}$$

For the typical values of Table I the bracketed quantity is 4.4 and $M_\theta=147$ amu. In general M_θ is increased by increasing D and/or decreasing s_0 and d. In the focused single-field system ($d=0$, $k_0=1$, $D=2s_0$) the bracketed quantity is 2. In addition to the improvement factor of 2.2 the double-field system has the advantage of requiring a much smaller pulsed voltage.

Over-All Resolution

The maximum resolvable mass, M, depends on the initial space and energy distribution functions. Although the exact problem is prohibitively difficult, upper and lower bounds on the value of M are easily established from the preceding analysis. It is clear that M

will be smaller than either M_s or M_θ. On the other hand it will be at least as large as the value, $M_{s,\theta}$, obtained by assuming the total time spread to be the sum of the energy and space time spreads,

$$\frac{1}{M_{s,\theta}}=\frac{1}{M_s}+\frac{1}{M_\theta}. \tag{12}$$

As an example, for the values of Table I, $M_s=400$ and $M_\theta=147$ so that $M_{s,\theta}=108$. Thus the maximum resolvable mass, in this case, lies between 108 and 147 amu. If we assume the smaller value, then mass 100 has a total time spread of $100/108=0.926$ times the time spacing (0.038 μsec) between masses 100 and 101. Hence, mass 100 has a time spread of 0.036 μsec of which 0.01 μsec (i.e., $0.038\times100/400$) is due to initial space distribution and 0.026 μsec is due to initial energy distribution. Higher masses may be resolved by using a longer free flight path and higher energy as well as by the use of time lag focusing which is discussed below.

Choice of Parameters

We now have enough information to justify the choice of, and indicate the limitations on, the typical values given in Table I. The size of the initial space and energy distributions are made as small as possible consistent with the desired intensity and source conditions. In our example we assume Δs cannot easily be made less than 0.2 cm. In general the initial energy of the ions is primarily thermal energy. The value $U_0=0.09$ ev represents the upper limit of the thermal energy of 98% of the ions at an effective source temperature of 227°C. The length D, which is essentially the length of the spectrometer, is limited by ion loss due to velocity components normal to D as well as by the desirability of having a compact system. The ratio d/s_0 is made small to obtain maximum energy resolution. The minimum size of d is limited by the possibility of electric field leakage through the grids, which might accompany excessive E_d. The value of s_0 is made somewhat larger than Δs, to give the good space resolution of Eq. (9).

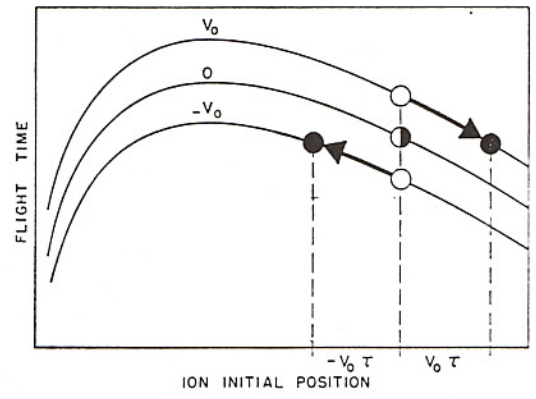

FIG. 3. Curves of flight time *versus* initial position used in the discussion of time lag focusing.

Energy resolution, which according to Eq. (11) requires that k_0 be large, indirectly requires as small a value of s_0 as possible by the focus condition, Eq. (5). The voltage to produce the total energy, U_t, is a compromise. Large voltages imply good energy resolution, but excessive voltages would complicate the electronic problem of providing the total voltage, or the fraction of it, that is necessary to produce E_s. A further electronic limitation might be the ability of an electronic detector to separate adjacent masses if the flight time became too short.

Time-Lag Energy Focusing

Energy focusing can also be produced by introducing a time lag, τ, between the formation of the ions and the application of the accelerating pulse. The potential well of the ionizing electron beam (about a few tenths of an electron volt) is sufficient to trap most of the ions until the beam is shut off. During the lag period, the ions, because of their initial velocities, move to new s positions. At a sacrifice of part of the space resolution, the lag and E_d/E_s ratio may be chosen so that most of the energy time spread is eliminated.

The focusing effect of lag can be explained with the aid of Fig. 3 where T is plotted *versus* s with initial velocity as parameter. Without lag three ions initially at the same initial position but with velocities 0 and $\pm v_0$ would have the flight times indicated on the curves by the open circles. During the lag period each ion moves a distance $v_0\tau$ which produces a change in flight time of very nearly $(dT/ds)v_0\tau$. As the velocities remain the same, each ion moves on its own curve to a new position indicated by a black circle. If the initial energy effect is to be eliminated the change in flight time thus produced must compensate for the flight time difference with no lag between ions of velocity v_0 and 0. To a good approximation the latter is one-half turn-around time, Eq. (10), [i.e., $T(v_0,s)-T(0,s)=1.02mv_0/qE_s$]. Thus we require that

$$\frac{dT}{ds}v_0\tau+\frac{1.02mv_0}{qE_s}=0. \tag{13}$$

or

$$\tau=\frac{-1.02m}{qE_s\dfrac{dT}{ds}}. \tag{13a}$$

The proper time lag is proportional to $m^{\frac{1}{2}}$ (since dT/ds is proportional to $m^{\frac{1}{2}}$) but independent of the ions' initial velocity. From Eq. (13a), ion lag focusing is possible only if dT/ds is negative thus violating the space focus condition ($dT/ds=0$). The use of ion lag in a region of positive slope would produce defocusing.

The τ and dT/ds combination yielding the best overall resolution is a compromise between two extremes. If τ is quite small then dT/ds must be large so that space resolution becomes the limiting factor. If τ is too large

the ions travel too far during the lag time, and as dT/ds is only approximately constant, the energy effects are no longer eliminated. Further since dT/ds is in general very small only near a point at which it vanishes some ions might move into a region of positive slope thus producing defocusing. With large values of lag, high-energy ions hit the chamber walls and are lost. This can be an advantage as long as ion loss is not excessive. In the experimental spectrometer time lags in the range of 0 to 3 μsec are used.

Both the best compromise and the quality of the resulting resolution depend on the actual initial space and energy distributions. Lag systems give preferred treatment to energy resolution; and no lag systems, to space resolution. Hence, the best method of operating depends on the space and energy distributions encountered. In some cases the use of time lag focusing gives greatly improved resolution. In others it seems to make little difference.

THE EXPERIMENTAL MASS SPECTROMETER

The essential elements of the experimental mass spectrometer are shown schematically in Fig. 4. A magnetic electron multiplier, similar to those used by L. G. Smith,[7] is used to detect and amplify the mass groups. For ease of construction, the flight tube and ion source are constructed of brass. Vycor glass is used as insulation between the source electrodes.

The drift space is approximately 40 cm long. An oil diffusion pump equipped with a water-cooled baffle holds the drift tube pressure between 5×10^{-6} mm and 5×10^{-5} mm as indicated on a Philips gauge. A tungsten wire, 0.125 mm in diameter, serves as the filament. The electron beam passes through two collimating slits, 0.5 mm by 2.0 mm and thence into the ionization region. These slits are spaced 0.5 and 1.5 mm from the filament. The one nearest the filament also serves as a control grid for the beam. An axial magnetic field of about 300 gauss also helps to collimate the beam. An electron trap is provided and is biased to minimize backscattering of the electron beam. The three source electrodes are approximately 3 cm square, and the two grids, 0.5 cm by 1.0 cm. The width of the ionization chamber is usually 2 mm to 4 mm, with the electron beam offset toward the rear of the chamber. The accelerating region is ordinarily from 1 to 2 cm wide.

Since the ion cathode of the multiplier is several thousand volts negative with respect to ground, the ions are accelerated after passing through the screen separating the drift tube from the multiplier chamber. This type of multiplier was chosen for several reasons. First, it permits the use of a plane ion cathode which eliminates the ion transit time variations encountered with the curved ion cathode of the conventional electrostatic multiplier. Secondly, the device has a very small transit time spread which makes it possible to use a large number of low gain stages. Thus we have been able to use unactivated Be–Cu dynodes with a gain of about 2.2 per stage. Using unactivated stages provides a gain which is relatively stable and unaffected by exposure to air. The total gain of the multipliers used has ranged from 10^5 to 5×10^9, the high gain models allowing a direct connection to the plates of an oscilloscope. Distributed amplifiers are used in conjunction with the low gain models. The band width obtained with these multipliers has been sufficient to faithfully amplify our ion pulses which vary from 0.010 to 0.050 μsec at the half-height points.

To reduce the background caused by ions which wander out of the ionization region, the electron beam is pulsed on immediately before the ion accelerating pulse is applied. The beam is controlled by a 100 volt pulse lasting for 0.1 to 1 μsec on the electrode nearest the filament. By controlling the filament temperature, pulsed currents up to 500 μa can be obtained. The conductors enclosing the ionization region are ordinarily biased positively at approximately the total voltage while the filament is 50 to 100 volts more negative. The flight tube and source exit grid are at ground so that E_d is applied constantly. The backing plate is pulsed with a small positive voltage to eject the ions. This pulse is flat topped and lasts for approximately 1.5 μsec which permits the ions to reach the drift tube before the termination of the pulse. Although operation in this manner somewhat increases the danger of background ions, it reduces the electronic requirements of the source pulse, especially when operating with high ion energies.

During the development of the spectrometer, total ion energies between 200 and 2000 ev have been used. Depending upon this energy and the geometry, an ion accelerating pulse between 16 and 160 volts has been used. This pulse and the electron pulse have rise times of about 0.1 μsec. The fall time of the electron pulse is about the same, but the fall time of the accelerating

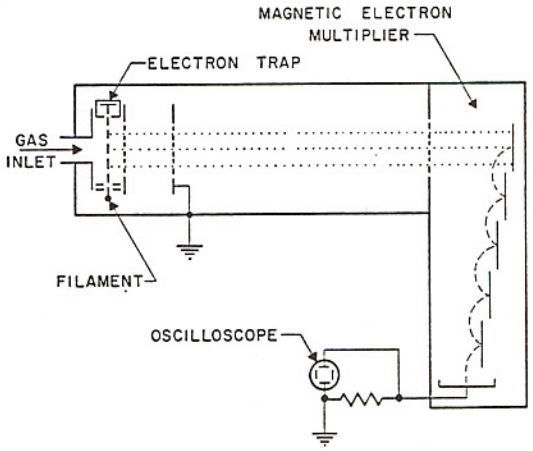

FIG. 4. Physical arrangement of the experimental TOF mass spectrometer.

[7] L. G. Smith, Rev. Sci. Instr. 22, 166 (1951).

pulse is immaterial since the ions have left the source before this pulse falls.

The repetition rate of the experimental model has varied from single shot operation to as high as 50 kc. The oscilloscope is synchronized to the ion accelerating pulse through a variable delay, so that any portion of the mass spectrum can be viewed.

EXPERIMENTAL RESULTS

Since the theoretical analysis is based on elementary principles, there was no need to test the basic theoretical results. However, experimental studies were needed to determine the initial space distribution, the initial energy distribution, the effects of space charge, and many minor construction details.

Although space charge effects are not large, they have produced a widening of the peaks observed on the oscilloscope. Experiments using baffles indicated that the effects which occurred took place in the flight tube rather than in the ion source. Another small perturbing factor was a slight leakage of the field, E_d, into the ionization region during ion formation. This was corrected by putting the source backing plate at a slightly negative potential with respect to the first grid. The required potential depends on the detailed structure of the first grid. The detected ion pulses begin to attenuate when the flight tube pressure reaches approximately 10^{-4} mm. However, the sharpness of the focus is relatively unaffected by chamber pressure. This result is believed to be due to the fact that ions which collide while traveling down the flight tube are usually scattered at angles which preclude their striking the ion cathode.

Considerable effort has gone into experimentally determining and understanding the initial space and energy distributions. These distributions were found by matching the observed resolution for different ion source conditions with the calculated resolution. For each different geometry (i.e., s_0, d, and D values), extensive numerical calculations were performed on an I.B.M. card program calculator for different space and energy distributions. The space distribution consistent with an entire series of tests for one electron gun is shown in Fig. 5. The initial energy distribution that agreed with the observations was a Maxwell-Boltzmann at 227°C. The type of agreement obtained is illustrated by the matched spectrum shown in Fig. 6 (the computed spectrum is based on the relative abundances given in the American Petroleum Institute Catalog of Mass Spectral Data).

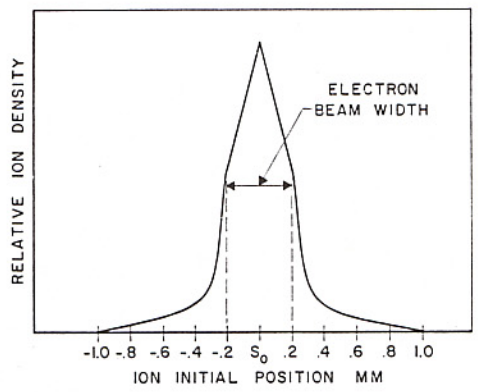

FIG. 5. Initial space distribution which gave the best correlation of computed and experimental spectra.

Time lag focusing was investigated experimentally. The most marked improvement in resolution obtained may be seen in Fig. 7 where the xenon spectrum for lag values 0, 1, and 2.5 μsec is shown.

PRECISE INTENSITY MEASUREMENTS

The detected intensity of a single mass group in a spectrometer depends on many spectrometer conditions

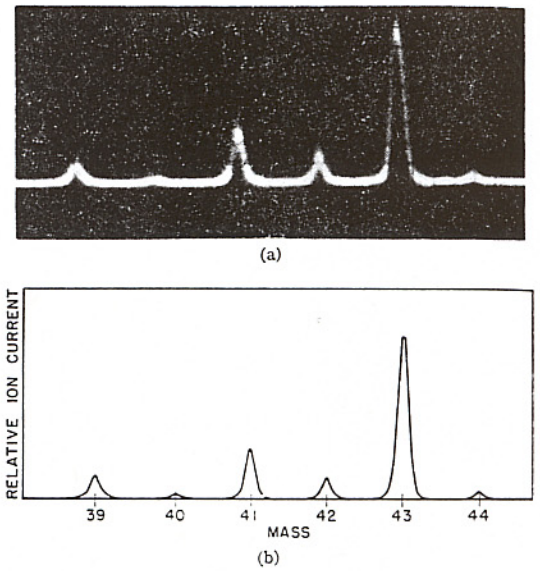

FIG. 6. Matched experimental and computed spectrum (*n*-butane components); from left to right masses 39, 40, 41, 42, 43, and 44 amu. The peak width is 0.024 μsec. (a) Experimental mass spectrum. (b) Computed mass spectrum.

which are difficult to control precisely (e.g., gas temperature and pressure, ionizing electron beam intensity, detector efficiency, etc.). However, to a good approximation, the ratio of two masses would be independent of most of these if both masses were measured from the same source pulse or even if they were detected on alternate source pulses.

We have measured intensity ratios by photographing single traces and found that ratios do indeed remain relatively constant even though wide variations are introduced in the intensity of ions. Although this measurement system is adequate for preliminary work, it actually is the limiting factor in making precise measurements for the following reasons:

(1) In order to reduce the focus stability required, the number of ions in a pulse is normally determined by a measurement of pulse area rather than pulse height.

Thus a tedious integration of each pulse is required, which entails rather careful photographic procedures to guarantee precision.

(2) Although measurements can be recorded quickly on film, they cannot be analyzed quickly.

(3) The accuracy attainable for small peaks is often limited by the number of ions of a given mass which are detected during each acceleration pulse. In order to obtain the necessary statistical accuracy, the results of many pictures must be analyzed separately and then combined.

In order to avoid these disadvantages, we have developed a multiplier which has, in addition to the final output electrode, two collectors which can be activated electronically. A mass peak is accepted by one of these collectors if a short duration pulse of 60 volts is applied to its "gating" electrode. The multiplier collector electrodes are each connected to integrating dc amplifiers. The amplifier outputs are connected to a recorder which directly records the ratio.

This electronic ratio recording system has been very successful in determining mass ratios and in investigating the factors which influence these ratios. Without any special regulation of source conditions, ratios have been constant over 24 hour periods to better than 1%. Tests have also been made on ratios when the ion intensity has been purposely varied by several hundred percent. Although some of these tests produced changes in the ratio, these ratio changes were always very small compared with the intensity changes. We are planning a detailed series of measurements of intensity ratios and shall report on these when they are complete.

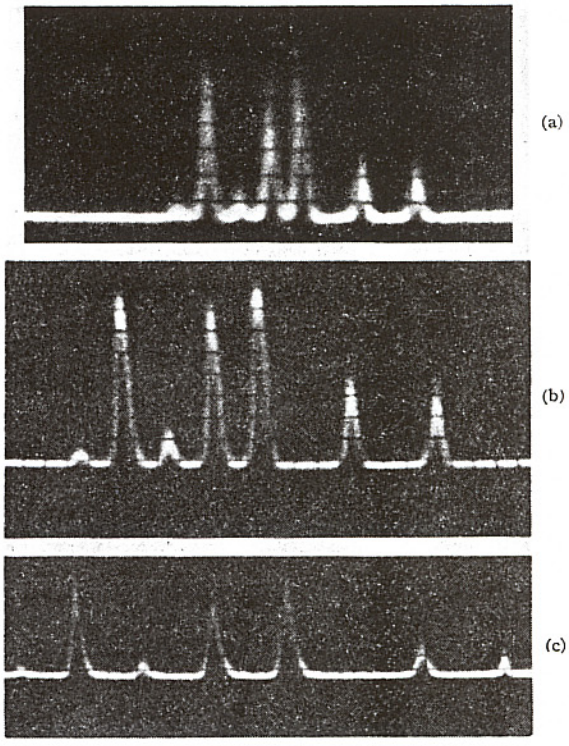

FIG. 7. Oscillograms of the mass spectrum of some xenon isotopes showing the effect of time lag focusing for lags (a) 0, (b) 1.0 μsec, and (c) 2.5 μsec; left to right masses 128, 129, 130, 131, 132, 134, and 136 amu. The sweep speed and gain were varied.

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