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New Time-of-Flight Mass Spectrometer*†

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A time-of-flight mass spectrometer based on principles previously described has been constructed with two major modifications to facilitate appearance potential measurements. These modifications are (1) an axial electron beam is pulsed through an ionization chamber utilizing techniques of Fox, *et al.*, and (2) a gated ion detector is employed to allow for integration of the resolved ion current from successive cycles. The instrument has been constructed of stainless steel to allow for measurements on chemically active gases. Theoretical resolution, limited by thermal energies of the ions, appears to be well over mass 200. Preliminary experimental work has verified this up to the region of mass 100. Ionization potentials, using the difference method, have been obtained from various gases that are in agreement with the spectroscopic data to within 0.05 volts.

INTRODUCTION

SINCE the ingenious method of Fox, *et al.*,[1] for precise measurements of appearance potentials with a mass spectrometer employs a pulsed ion source, a time-of-flight method of analysis is suggested. An examination of such instruments previously described[2,3] showed that (1) they suffered from severe requirements placed on the detector amplifier because of the rise time of the collector plate and (2) the small average ion currents produced by such instruments would not readily adapt to the new method. Further, with the geometry of Fox and his co-workers, the electron beam is at right angles to the ion beam and focused by a magnetic field in the region of the ion source. Extremely narrow electron-defining slits are necessary to reduce the energy spread in the electron beam which would otherwise result from excessive transverse motion of the electrons in the source magnetic field. As a result, the ion currents available are reduced by an order of magnitude over those obtained in a conventional source.

The elimination of the magnetic analyzer employed in deflection mass spectrometers permits the use of ion beams of large cross section, with a concomitant increase in the permissible size of the electron beam. It would then be expected that the usual limitations on ion currents imposed by the necessity of producing a tightly collimated ion beam could be eliminated and, in addition, an axial electron beam of large cross section could be utilized without the necessity of an ion-source magnetic field. The problem of poor resolution of earlier instruments can be traced to excessive capacitance in the collector plate, which does not permit the observation of individual pulses of resolved ion current. This difficulty can be eliminated by gating the ion beam with a pair of grids preceding the ion collector in such a manner that only ion bursts corresponding to an individual mass number reach the collector. The ion current from a large number of cycles is integrated and detected with a conventional electrometer amplifier.

The instrument to be described has (1) incorporated all the advantages inherent in the new method of appearance potential measurement, (2) produced larger ion currents than conventional instruments, (3) permitted the use of high-current electron beams whose energy is quite homogeneous, and (4) offered lighter and less expensive construction through the absence of all magnets.

DESIGN CONSIDERATIONS

A time-of-flight mass spectrometer is essentially a drift tube in which short pulses of ions are produced at one end at time zero, with either constant energy $\frac{1}{2}Nmv=U_0$, or constant momentum $NMV=P_0$, where N is the mass number, v the velocity, U_0 the energy, P_0 the momentum of the ions, and m the mass of a nucleon. At different times later, ions with different masses arrive at the end of tube. For the case of constant energy we have

$$t=l[MN/2U_0]^{\frac{1}{2}},$$

where t represents the time of flight of the ion from the source to the collector, and l is the length of the drift tube; whereas for the case of constant momentum we have

$$t=l[MN/P_0].$$

If the collector plate is made sensitive at time t for a period Δt, by opening the gating grids, then the highest number that may be resolved is given by

$$N/\Delta N=t/\Delta t \quad \text{for constant momentum}$$

and

$$N/\Delta N=\tfrac{1}{2}(t/\Delta t) \quad \text{for constant energy.}$$

It appears, therefore, that a constant momentum instrument would yield double the resolution of a constant energy instrument. However, within limits Δt can be

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† The basic principles of this instrument and the description of a first model were described in an Atomic Energy Commission report NYO-825 (July, 1952).

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[1] Fox, Hickam, Kjeldaas, and Grove, Phys. Rev. 84, 859 (1951).

[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).

made arbitrarily small, so this is not the fundamental limitation. In either instrument, thermal velocities limit the accuracy with which an ion beam will remain bunched.

Taking the constant momentum case first, the velocity of ions of the same mass will vary from v_0, the velocity imparted by acceleration, by $\pm v_t$ the thermal velocity,

$$v_t=[2U_t/mN]^{\frac{1}{2}},$$

where U_t is the thermal energy. For constant momentum, we define an effective energy

$$U_{eff}=P_0^2/2mN.$$

Then the time spread in the ion pulses resulting from thermal velocities will be

$$\delta t=\pm(U_t/U_{eff})^{\frac{1}{2}}t_0,$$

since $V^{\propto}U^{\frac{1}{2}}$. Since the permissible timing error for masses differing by ΔN is $\Delta t=\Delta Nt/N$, we obtain by setting $\Delta t=2\delta t$,

$$\Delta N/N=2[U_t/U_{eff}]^{\frac{1}{2}}.$$

However, in the constant energy case the thermal velocities add as energies, or $U=U_0\pm U_t$;

$$t=\frac{l}{[(2U_0\pm U_t)/MN]^{\frac{1}{2}}}=\frac{t_0}{[1\pm(U_t/U_0)]^{\frac{1}{2}}}.$$

Expanding by the binomial formula, assuming $U_t\ll U_0$, $t=t_0[1\mp\frac{1}{2}(U_t/U_0)]$.

Since $\delta t=(t-t_0)$,

$$t=\tfrac{1}{2}(U_t/U_0)t_0,$$

or, again setting $\Delta t=2\delta t$, $\Delta N/N=2\Delta t/t=2U_t/U_0$. Note here that the factor of two does not disappear, but the square root is not present. Clearly, the resolution is higher for the constant energy case. To calculate the necessary U_0 or U_{eff}, assume $U_t\sim 0.1$ electron volts. If $\Delta N/N=1/300$, then $U_0\gtrsim 60$ electron volts (const. E) and $U_{eff}\gtrsim 36\,000$ electron volts (const. P) As this figure does not seem practical, a constant energy scheme with $U_0\gtrsim 60$ electron volts is employed.

To prevent the ion beam from spreading laterally as a result of thermal velocities, either some form of focusing must be used or the transit time kept short enough. As a small transit time is antagonistic to a good resolution we shall consider it more carefully. The condition for no loss of ion beam intensity caused by lateral spreading may be written as follows:

$$(2U_t/mN)^{\frac{1}{2}}t_0<r,$$

where r is the radius of the collector plate. Since $t=l/V_0$, this becomes $[U_t/U_0]^{\frac{1}{2}}l<r$ or $r/l>[U_t/U_0]^{\frac{1}{2}}$. If $r=2$ cm, $l=100$ cm, and $U_t\sim 0.1$ electron volt, then $U_0\gtrsim 250$ electron volts.

An instrument to resolve mass number 100 from its neighbors would have to have $\Delta N/N$ equal to 0.01. With a one-meter flight path, this requires Δt to be less than 0.1 μsec, if the above criterion for complete transmission is to be fulfilled. As this is capable of being realized with existing electronic techniques, these parameters were adopted for the instrument constructed.

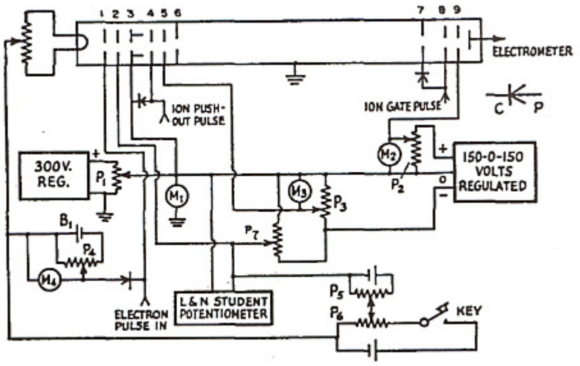

Fig. 1. Schematic representation of the time-of-flight mass spectrometer.

The requirements on the source are the same as in any other mass spectrometer; however, if the new method of Fox is to be utilized to its fullest, precautions to insure good parallel geometry (and hence uniform fields) must be taken. For this reason, as well as for simplicity of construction, an axial electron beam source has been used.

The electron beam is accelerated through the ionizing region into a region of high retarding field which brings the beam to rest and returns it through the ionizing region. Utilizing large parallel plates to mount accelerating grids permits the geometry to be made optimum without the use of narrow electron defining slits. This should permit orders of magnitude of increase in the electron and ion currents employed.

OPERATION

A schematic representation of the over-all instrument is shown at the top of Fig. 1. The ion source consists of a set of parallel grids, numbered one through six, following a heated tungsten filament. Grid 1 is used to gate the electron beam on during the electron bombardment period. Grid 2 is used to provide a retarding field to cut off the electron energy distribution following the method of Fox *et al.* The space between grids 3 and 4 is free of all fields, and acts as the region for ionization. After the electron stream is cut off, an electrical pulse applied to grid 4 is used to push the ions out of the ionizing region and is hereafter called the ion pushout pulse. Grid 5 is maintained at a high negative potential to repel the electrons after they have passed through grids 3 and 4. This potential also serves to produce a high initial accelerating field for the ion bunch formed between grids 3 and 4 and ejected by the ion push-out pulse, helping to eliminate undesired time delays in the ion source with a resulting improvement in mass resolution. Grid 6, maintained negative with respect to the ionizing chamber, is included to fix the energy the ion bunch acquires before entering the drift tube.

The collector system consists of three grids and a

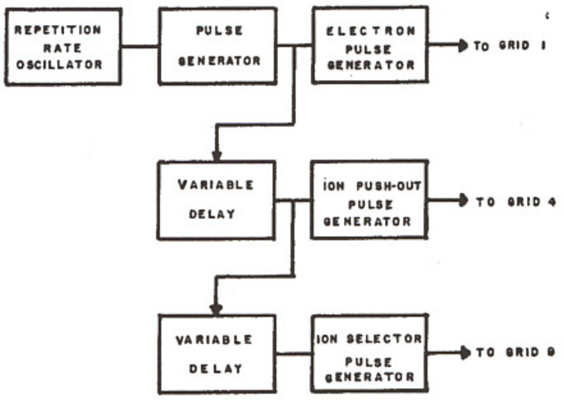

FIG. 2. Block diagram of timing circuitry.

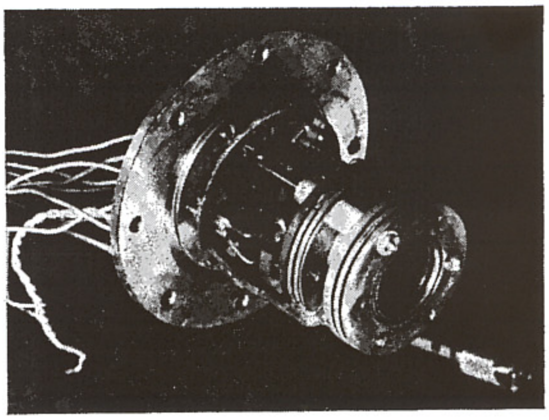

FIG. 3. Photograph of ion source.

collecting plate. The first grid, 7, is connected to the drift tube to maintain this region at a uniform potential. The second grid, 8, is pulsed with a very high narrow pulse, hereafter called the ion selector pulse, to select a single mass bunch. The third grid, 9, carries a retarding potential sufficient to reject any ion not receiving both the ion draw-out pulse and the ion selector pulse. The potential on grid 9 is also variable to allow for measurement of initial kinetic energy of dissociation following the method of Hagstrum.[4] The large positive potential on grid 9 also serves to collect secondary electrons from the collector.

A block diagram of the timing circuitry is shown in Fig. 2. The repetition rate oscillator produces 5000 pulses per second, which allows an ample interval to insure that all ions due to one pulse are collected before a new pulse is produced. The pulse from the rate oscillator is sharpened and fed into the electron pulse gate generator and to the ion pulse delay generator. The electron pulse length and the ion pulse delay are produced by two univibrator gate generators, each independently variable from two to twenty microseconds. The output from the delay generator is differentiated, inverted, and used to trigger the ion pushout pulse generator and the ion selector pulse system. The width of the ion pushout pulse is about 0.2 μsec and is variable in height from zero to fifty volts. The 0.1-μsec ion selector pulse must be stable, precisely adjustable in time, and free of jitter to the extent of 0.05 μsec.

The dc potentials for operating the tube are obtained from voltage dividers across conventional regulated power supplies. Figure 1 is a schematic representation of the way in which these voltages are impressed. The main accelerating voltage is established by potentiometer P_1, across a negative grounded supply and is applied to grids 3 and 4. Meter M_1 monitors this potential difference. Electron-accelerating potential from P_7 is applied between grids two and three. This voltage is monitored by a volt-box and potentiometer, and represents the quantity varied in taking an appearance potential curve. A retarding potential applied to grid 2 from potentiometer P_5, is supplied by a dry battery with a key provided for inserting a small increment of voltage from potentiometer P_6 in obtaining a "difference ion current" as described by Fox *et al.* Grid 1 is biased about 5 volts negative with respect to the filament by P_4 with the positive gating pulse for the electron beam superimposed. The negative ion pushout pulse is applied to grid 4, which is normally clamped to grid 3 with a germanium diode. Thus, while the electron beam is on, grids 3 and 4 form a field-free region for ionization. Grid 5 is maintained negative by P_3 with respect to the filament and helps to eliminate time delays in getting the ions out of the ionizing region. This voltage is not critical but is usually set at about 100 volts on meter M_6. The final grid 6 in the ion source structure is grounded to the tube shell and serves to render the drift tube a unipotential region. The same function is fulfilled by grid 7 in the ion collector assembly. The ion selector pulse and the retarding potential from potentiometer P_2 are applied to grid 8 and the retarding potential from potentiometer P_2 is applied to grid 9.

CONSTRUCTION

The instrument was constructed in a 1-meter length of $2\frac{1}{2}$ in. i.d. stainless steel pipe. A "*T*" at the source end, of the same material, provides a high speed pumping lead for the source. The "*T*" is connected to a cold trap and a VMF-260 diffusion pump. An ionization

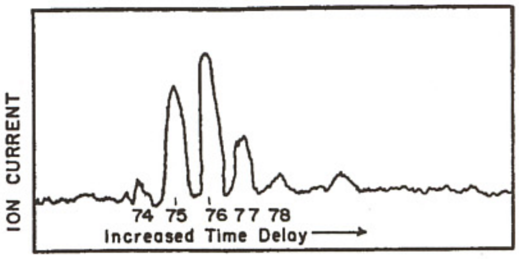

FIG. 4. Background mass spectrum in the vicinity of mass 75.

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[4] H. D. Hagstrum, Revs. Modern Phys. 23, 185 (1951).

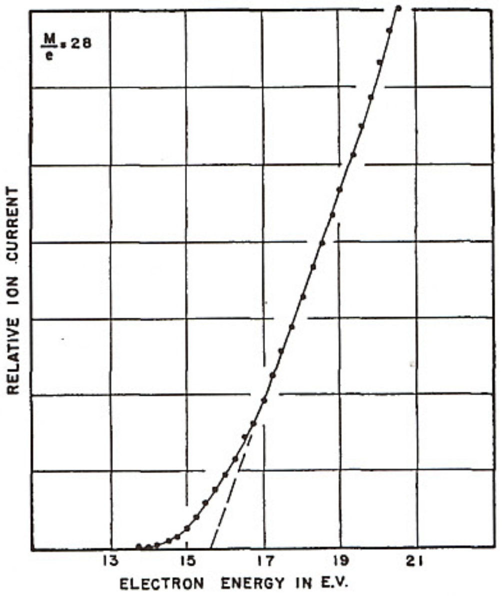

FIG. 5. Ionization efficiency curve for argon.

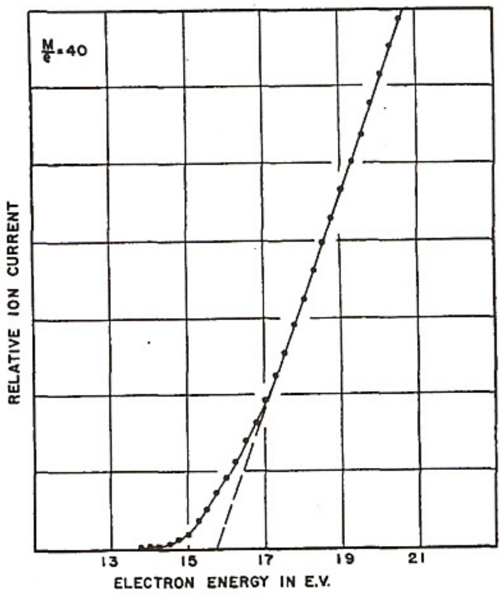

FIG. 6. Ionization efficiency curve for nitrogen.

gauge in the pumping line permits pressure measurements. The source and collector units are mounted on plates which bolt to flanges on the end of the tube. Figure 3 shows the source mounting. Removal of the source or collector is thus adequately provided for without breaking of electrical connections. The tube is maintained at an elevated temperature to reduce background by a noninductive Nichrome *V* ribbon heater winding around the entire length of the tube. All gaskets are of teflon. The tube temperature can be maintained at 350°C, though 100°C is the normal operating temperature. The source and collector assembly consists of $2\frac{1}{4}$-in. Nichrome *V* plates with 1-in. opening covered with tungsten of 120 meshes per inch. This material, suggested by Bennett[5] in his rf spectrometer, is supplied in a form of a flattened sleeve and is in a state of strain. Careful steps had to be taken to mount the mesh flat despite its curling tendencies. The source was assembled by stacking the grids on six Nichrome *V* 4–40 threaded rods with lavite spacers to separate the grids. Each rod contacts one plate by means of a copper nut pressed into the appropriate hole in the grid plate. The filament stem is supported from the bottom grid by a small stainless steel block and set screw. A 0.015-in. tungsten filament operated at 15 amp was used. A suitable emission was obtained with a negligible voltage drop across the emitting portion of the filament. A small nickel shield behind the filament, connected electrically to it, removed the problem of electrons from the filament being collected on the lead wires and other electrodes.

TABLE 1. Ionization potential of several molecules as determined by the "vanishing difference current" method of Fox, *et al.*

Compound	Mass	Ionization potential in volts for five trials				Average	Spectroscopic values
Xenon	132	12.31	12.12	12.19	12.20 12.13	12.19	12.14
Carbon dioxide	44	13.88	13.81	13.68	13.87 13.75	13.80	13.79
Nitrogen	28	15.60	15.70	15.63	15.62 15.54	15.62	15.58
Argon	40	15.80	15.81	15.80	15.72 15.75	15.77	15.77

RESULTS

The instrument was built and put into operation. Figure 4 shows a typical spectrum that was obtained due to background in the region of mass 75. We note a five-fold improvement of resolution over previously described time-of-flight instruments. Thus the instrument appears to be satisfactory, as an analytical tool, at least up to mass 100. No attempt was made to maximize the resolution and the analytical properties were not further pursued up to this date.

Figures 5 and 6 are ionization efficiency curves for argon and nitrogen respectively. These curves are obtained by varying P_7 as described earlier. A linear extrapolation gives a value for the ionization potential, on an absolute scale, within 0.1 volts of spectroscopic data.

Table 1 shows the results obtained for the ionization potential of xenon, carbon dioxide, nitrogen, and argon. No actual ionization efficiency curves were taken, but a point was simply looked for at which the difference current vanished when the key as shown in Fig. 2 was closed. Results so obtained gave values to within 0.05 volt of spectroscopic data.

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[5] W. H. Bennett, J. Appl. Phys. **21**, 143 (1950).