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REEXAMINATION OF RADIOFREQUENCY MASS  
SPECTROMETERS - Center Director's Discretionary  
Fund Final Report

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Science and Engineering Directorate

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16. ABSTRACT  The three-stage, two-cycle, Bennett mass spectrometers in use in space and ground experiments today is of the same physical configuration as developed by Bennett in 1950. Sine-wave radiofrequency (RF) is also still used. The literature indicated that the electronics and physical manufacturing capabilities of 1950 technology may have limited the use of other improvements at that time. Therefore, a study, experimental and analytical, was undertaken to examine previously rejected RF approaches as well as new ones. The results of this study indicate there are other approaches which use fewer grids and square wave or a combination of square-wave and sine-wave RF. In regard to suppression of harmonics, none performed better than the three-stage, two-cycle, Bennett mass spectrometer. Use of square-wave RF in the Bennett approach can provide a slightly more compact configuration but no increase in throughput.					
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TABLE OF CONTENTS

	Page
INTRODUCTION .....	1
BENNETT MASS SPECTROMETER .....	1
OTHER RF APPROACHES .....	5
Previous Approaches Examined.....	5
New Approaches.....	7
EXPERIMENTAL INVESTIGATION .....	15
SUMMARY .....	20
REFERENCES .....	21
APPENDIX.....	22

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## LIST OF ILLUSTRATIONS

Figure	Title	Page
1.	Single Bennett stage .....	2
2.	Standard three-stage two-cycle Bennett mass spectrometer .....	4
3.	Ion transit of Bennett mass spectrometer stage with square RF applied .....	6
4.	Ion transit of a split Bennett stage with square RF applied .....	7
5.	Standard mass spectrometer energy gain versus mass for designed phase of entry .....	7
6.	Mass spectrometer energy gain versus mass .....	8
7.	Square-wave RF Bennett mass spectrometer energy gain versus mass .....	10
8.	Square-wave RF Bennett mass spectrometer energy gain .....	11
9.	Diagram illustrating single acceleration mass spectrometer with quasi field-free drift .....	12
10.	Energy gain curve .....	13
11.	Diagram indicating hybrid Bennett approach .....	14
12.	Energy gain curve for hybrid Bennett .....	15
13.	Experimental arrangement .....	16
14.	RPA curve with Bennett stage RF on and off .....	16
15.	Experimental data showing primary and harmonic for a standard Bennett mass spectrometer .....	17
16.	Experimental data of Bennett mass spectrometer .....	18
17.	Vacuum system background .....	18
18.	Data indicating integral cycle transmission of ions in the hybrid approach .....	19

## NOMENCLATURE

<u>Terms</u>	<u>Definition</u>
d	distance
D	field-free drift space distance. $D_1$ denotes first drift space encountered by an ion, etc.
e	electronic charge
E	electric field value
$E_0$	value of maximum electric field associated with maximum potential on RF grids due to sine-wave signal
F	force on an ion due to electric field
m	mass of an ion
N	number of integral RF periods for the selected mass ion in a mass spectrometer to cover a drift distance D
n	summation term in Fourier series
RF	radiofrequency
s	distance separating two grids in a mass spectrometer RF stage where one grid is at a set potential and the other has an RF signal applied. In the standard Bennett stage, a distance $2s$ separates the two grids at a fixed potential.
v	ion velocity
V	electric potential
$V_a$	potential through which ions are accelerated into the mass spectrometer systems
$V_{RF}$	maximum peak to peak potential of sine-wave RF signal applied to RF grids
t	time
W	energy gain or loss in mass spectrometer system. Generally given in this report in eV units.
$\alpha$	set phase of $72/180 \pi$ for one mass spectrometer approach
$\beta$	set phase of $36/180 \pi$ for one mass spectrometer approach
$\delta$	RF phase at ion entry into mass spectrometer RF stage
$\omega$	angular frequency of applied RF signal

NOMENCLATURE (Concluded)

<u>Subscripts</u>	<u>Definition</u>
1	first encountered
2	second encountered
sin	used to designate values associated with the sine-wave portion of a mass spectrometer approach which utilizes both square- and sine-wave RF

## TECHNICAL MEMORANDUM

### REEXAMINATION OF RADIOFREQUENCY MASS SPECTROMETERS Center Director's Discretionary Fund Final Report

#### INTRODUCTION

Techniques for determining the mass constituents in a neutral or ionized gas have been presented in the literature. Some have been developed to a sophisticated state and are used routinely both in the laboratory and as space flight instruments. The literature contains descriptions of many different mass analysis techniques, most of which date from the 1950's. At that time, a major factor in determining which techniques were developed into a useful instrument depended on the electrical and mechanical requirements of the approach. In the last 30 years significant advances in both of these areas have been made so that reexamination of previously undeveloped approaches may provide insight into producing better radiofrequency (RF) mass spectrometers.

The magnetic-sector and quadrupole-type mass spectrometers were not considered in this study. They have been developed to a high level of sophistication and improvements in mechanical manufacturing has been incorporated into these devices. The advantage of the RF type of mass spectrometers is their simplicity, their high throughput, and their ability to collect measureable current without using multipliers and high voltage. The Bennett mass spectrometer introduced in 1950 is still in use today [1]. The electronics have improved and the wire mesh for the grids is much finer and more uniform, but the configuration is exactly like the Bennett mass spectrometer of 1950 [2,3]. Therefore, a reasonable question seems to be: Can the configuration be changed to take advantage of the advances in technology? This question is addressed in this report.

#### BENNETT MASS SPECTROMETER

The first practical RF mass spectrometer was introduced by Bennett in 1950 [1]. In order to consider variations on his approach and other RF mass spectrometer designs, the Bennett mass spectrometer design will first be discussed.

A single stage of the Bennett mass spectrometer consists of three equally spaced, parallel plane grids of fine wire mesh, as shown in Figure 1. The outer two grids are maintained at a set potential and an RF field is applied to the center grid. The set potential may be selected to accelerate a specific ion population into the stage at a given velocity. A varying electric field,

$$E = E_0 \sin(\omega t + \delta) ,$$

exists between the first two grids. The electric field between the second and third grids is

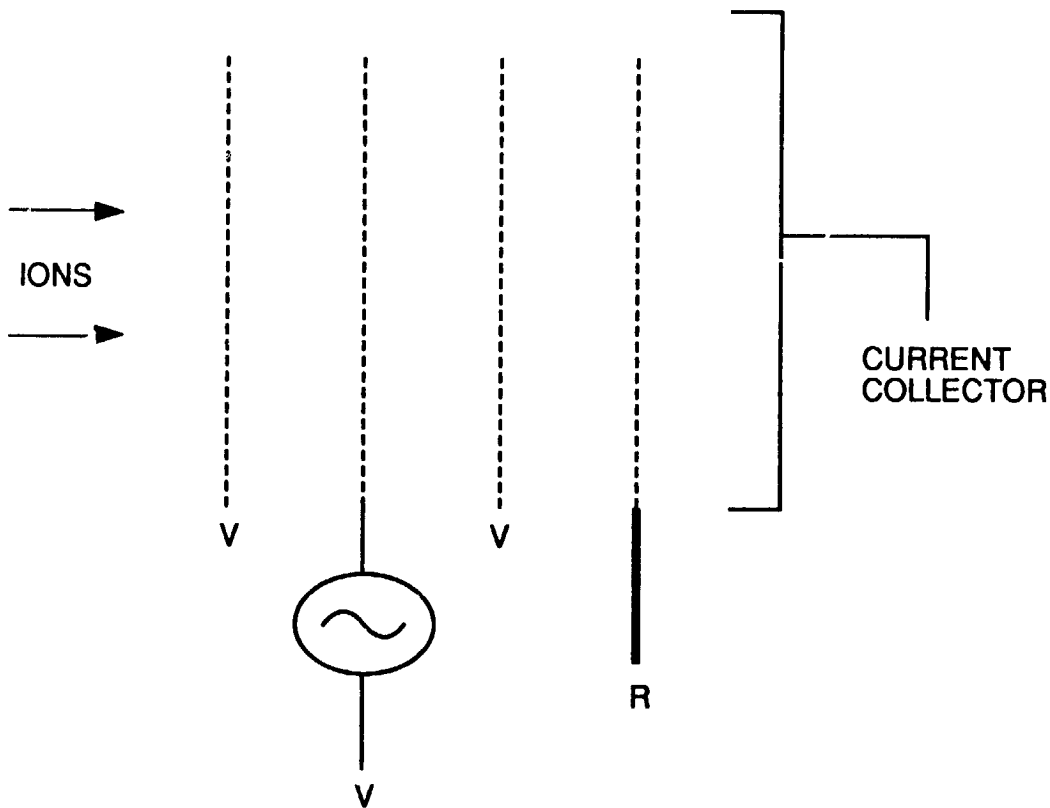


Figure 1. Single Bennett stage. (RF potential is applied to the middle grid, relative to the first and third grid. A retarding potential stops all ions except those which gained the maximum energy.)

$$E = -E_0 \sin (\omega t + \delta) .$$

If an ion enters with the right velocity and phase it will cross the center grid just as the RF potential is changing polarity and it will gain energy in the regions between grids one and two and two and three.

The energy acquired by an ion crossing two grids with an RF field applied to the second is given by

$$W = v \int F dt , \tag{1}$$

where  $F$  is given by the charge of the ion times the electric field. Therefore, the energy gained by an ion transiting a single Bennett stage is

$$W = v \left[ \int_0^{s/v} E_0 e \sin (\omega t + \delta) dt + \int_{s/v}^{2s/v} -E_0 e \sin (\omega t + \delta) dt \right] ,$$



or

$$W = \frac{E_0 e v}{\omega} \left[ \cos \delta - 2 \cos \left( \frac{s\omega}{v} + \delta \right) + \cos \left( \frac{2s\omega}{v} + \delta \right) \right], \quad (2)$$

with

$$E_0 = \frac{V_{RF}}{2s}.$$

There is a maximum in energy gained by an ion when the condition

$$\frac{s\omega}{v} + \delta = \pi = 180 \text{ deg}$$

is fulfilled. Equation (2) is a maximum with respect to variations in  $\omega$  when [1]

$$\frac{s\omega}{v} = 2.33,$$

and, therefore,  $\delta = 0.81$ . Any ion which enters the Bennett stage, does not enter with the right phase relative to the RF, and does not have the right velocity will gain a lesser amount of energy and may lose net energy as it traverses the region. If all the ions entering the Bennett stage have been accelerated to the same energy they will have different velocities due to their mass difference. A retarding grid following the Bennett stage will repel the ions not receiving the maximum energy. By sweeping the RF or the accelerating potential, the condition for maximum energy gain will occur for different masses and the result is a mass spectrometer instrument. The angular frequency at which a selected ion will gain maximum energy is,

$$\omega = \frac{2.33}{s} \sqrt{\frac{2 e V_a}{m}},$$

where it is assumed the velocity of the ion is totally due to the energy gained by accelerating the ion into the stage.

An examination of the resolution of a single Bennett stage indicates it is poor. In order to provide sufficient resolution, a mass spectrometer of three stages separated by two field-free drift regions was designed by Bennett and has become the standard configuration [1,2,3]. It is illustrated by Figure 2. The drift region allows separation of the ions which travel through the previous stage with the same phase and have similar gains in energy. The separation will occur due to the different ion velocities. This way only the ions of the selected mass will enter the next stage at the optimum phase. It can be shown that the distance between the two sine-wave RF grids in two Bennett stages, separated by a drift region, must be

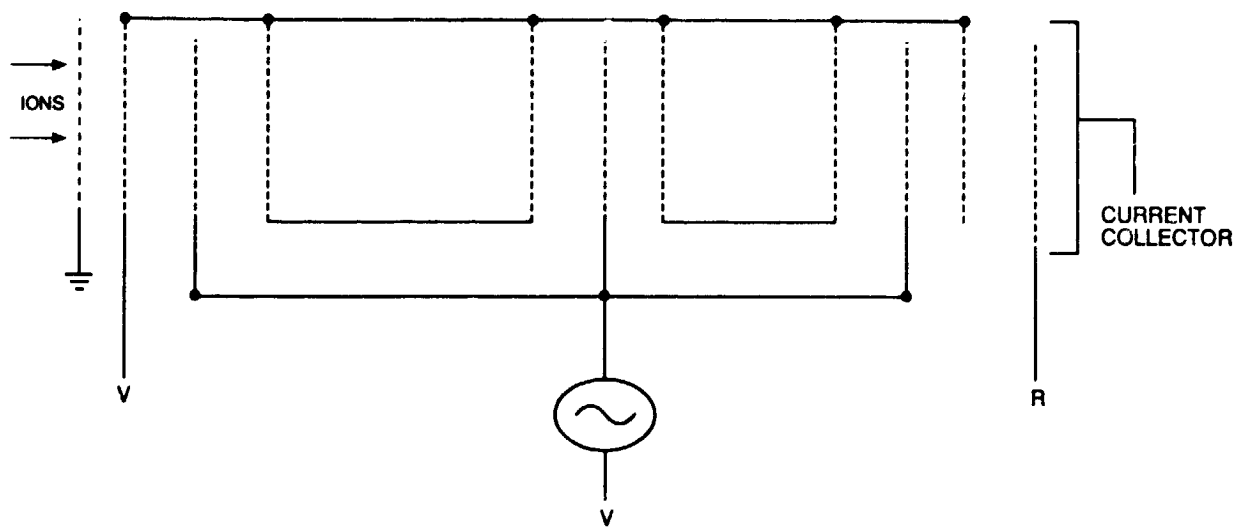


Figure 2. Standard three-stage two-cycle Bennett mass spectrometer.  
 (The standard Bennett mass spectrometer is made up of three stages as shown in Fig. 1 separated by drift regions.)

equal to  $2.695 N s$  in order for the favored ion to arrive at the next stage with the proper phase.

For an ion to gain maximum energy from both stages, it must maintain a proper phase with the RF such that it crosses the RF grid of each stage just when the RF is changing polarity. Therefore, the time to travel between two RF grids is an integral number of wavelengths. Now,

$$d = v t \quad ,$$

and

$$d = \sqrt{\frac{2 e V_a}{m}} \frac{2 \pi N}{\omega} \quad ,$$

therefore,

$$\omega = \frac{2 \pi N}{d} \sqrt{\frac{2 e V_a}{m}} \quad .$$

Comparing this with the above given equation for  $\omega$ , it can be seen that,  $d = 2.695 N s$ . The field-free drift distance (as can be seen in Fig. 2) is therefore,

$$D = (2.695 N - 2) s \quad .$$

The energy gain in a three-stage Bennett mass spectrometer can be obtained by integrating in a manner similar to the single stage. The result is

$$\begin{aligned}
 W = \frac{v V_{RF}}{s \omega} & \left[ \cos \delta - 2 \cos \left( \frac{s\omega}{v} + \delta \right) + \cos \left( \frac{2s\omega}{v} + \delta \right) + \cos \left( \frac{(2s + D_1)\omega}{v} + \delta \right) \right. \\
 & - 2 \cos \left( \frac{(3s + D_1)\omega}{v} + \delta \right) + \cos \left( \frac{(4s + D_1)\omega}{v} + \delta \right) \\
 & \left. + \cos \left( \frac{(4s + D_1 + D_2)\omega}{v} + \delta \right) - 2 \cos \left( \frac{(5s + D_1 + D_2)\omega}{v} + \delta \right) \right] . \quad (3)
 \end{aligned}$$

This expression for energy gain  $W$  and all subsequent expressions is given in units of eV.

In the mathematics presented, the assumption is made that the velocity gained through the mass spectrometer is insignificant compared to the initial velocity. In practice, this is not always the case and a retarding potential is applied between stages equal to the energy gained in the stages, so that the ions, which will gain maximum energy, actually maintain their energy through the mass spectrometer.

## OTHER RF APPROACHES

### Previous Approaches Examined

Besides the Bennett mass spectrometer there were many other RF-type of approaches which were investigated [4]. The problem with all RF approaches is harmonics. That is, there are other ions with velocities and phase entry into the RF field which still gain nearly all of the maximum energy. The Bennett is the best RF approach at being able to deal with these harmonics. Still, the retarding grid potential necessary to get rid of harmonic peaks reduces the spectrometer sensitivity because some of the favored ions are also repelled. All of the ions of the mass, for which the Bennett spectrometer is set, do not reach the collector, only those which enter the instrument with the proper phase relative to the RF. This can be a small percentage. As the favored ions enter farther from the optimum phase they gain less energy. If the retarding potential must be set close to the maximum energy gain to suppress harmonics, then the selected ions which enter at a non-optimum phase will also be repelled. Other researchers have devised schemes which do sample all of the ions of the selected mass [5,6]. This can increase the sensitivity significantly but they also have strong harmonics which cannot be reduced.

Reference 4 provides an excellent collection of RF mass spectrometer approaches and discusses them in some detail. In the approaches compared in Reference 4, the Bennett is the favored RF approach. Other researchers also considered improvements to the Bennett mass spectrometer [7-10]. Henson proposed that a single Bennett stage be modified by making the RF grid actually two grids with a drift region between them [7]. He proposed that a square wave, for greater resolution, be

applied to these center grids and that this system has an improved resolution. Others also proposed that a sawtooth or square-wave RF signal will provide greater resolution. These and other possible improvements will be discussed.

The improvement offered by Henson at first appears reasonable. It was referenced often and lauded as a significant improvement [4]. However, a close look points out a problem with it and the use of square or sawtooth type wave functions. In the standard Bennett, the ion does not gain an energy equal to the maximum amplitude of the RF because of the sine-wave shape. The sine-wave maximum amplitude is removed in phase from the point at which it changes polarity. Therefore, as discussed earlier there is one phase with which an ion of the proper velocity must enter a three-grid Bennett stage in order to gain maximum energy. For a single Bennett stage with square-wave RF, ions of different velocities can receive the maximum energy if they enter with a phase such that they arrive at the center grid as the RF changes polarity. There is a phase for each ion which is less massive than the one which traverses the stage in one RF period such that it will also gain the maximum energy. Figure 3 shows how three ions of different velocity will all gain the maximum energy if they pass through a single Bennett stage where square RF is applied and if they all cross the center grid as the polarity is changing. The approach proposed by Henson has a drift region separating the positive and negative portion of the RF. Therefore, ions of different velocities will be able to move through the drift region in different integral RF periods and still gain maximum energy. Figure 4 illustrates these points. The danger is that resolution is increased at the expense of increased number of harmonics and their amplitude. Sawtooth RF is impossible to consider since increasingly faster ions will see the potential across the gap approaching a dc potential and gain an energy approaching the sawtooth amplitude.

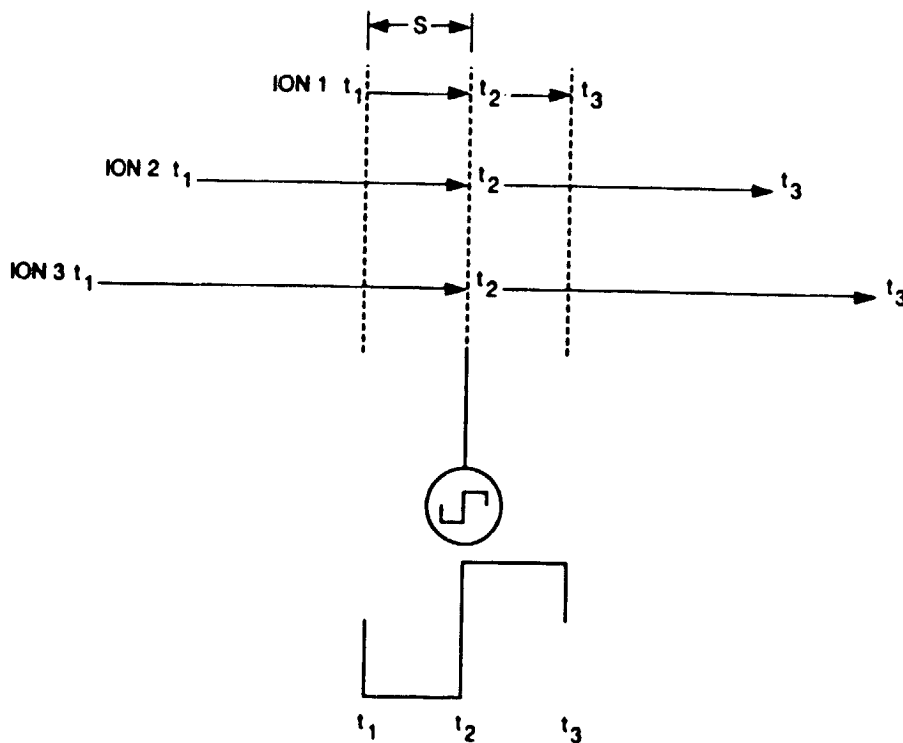


Figure 3. Ion transit of Bennett mass spectrometer stage with square RF applied. (Notice that a faster ion can also gain the maximum available if it enters at a different phase relative to the RF.)

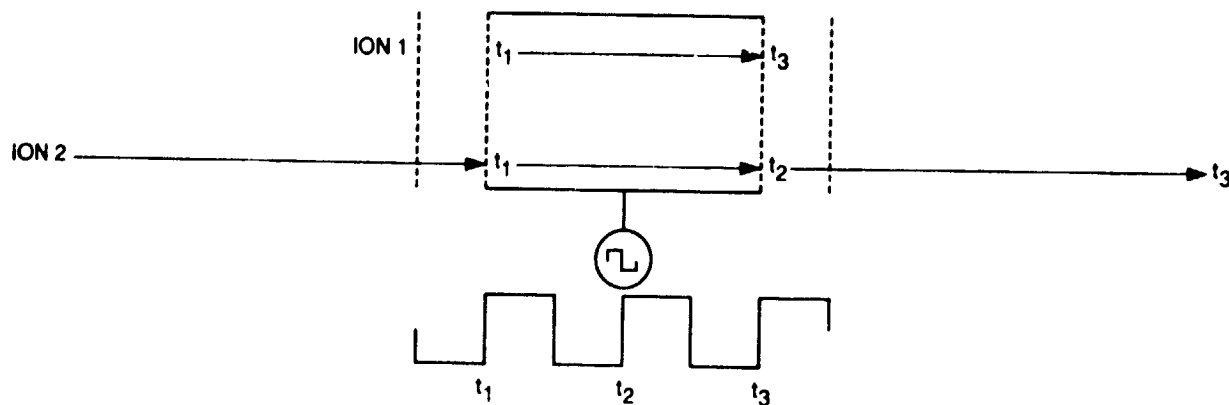


Figure 4. Ion transit of a split Bennett stage with square RF applied. (Resolution of this single stage is improved but, as seen in Fig. 3, faster ions can gain the maximum energy available if they enter with the right phase.)

### New Approaches

#### Bennett Mass Spectrometer with Square-Wave RF

Figure 5 is the energy gain curve as a function of mass for ions of an equal energy entering a three-stage two-drift space (referred to as two cycle) standard Bennett mass spectrometer. This is the curve typically shown in the literature for

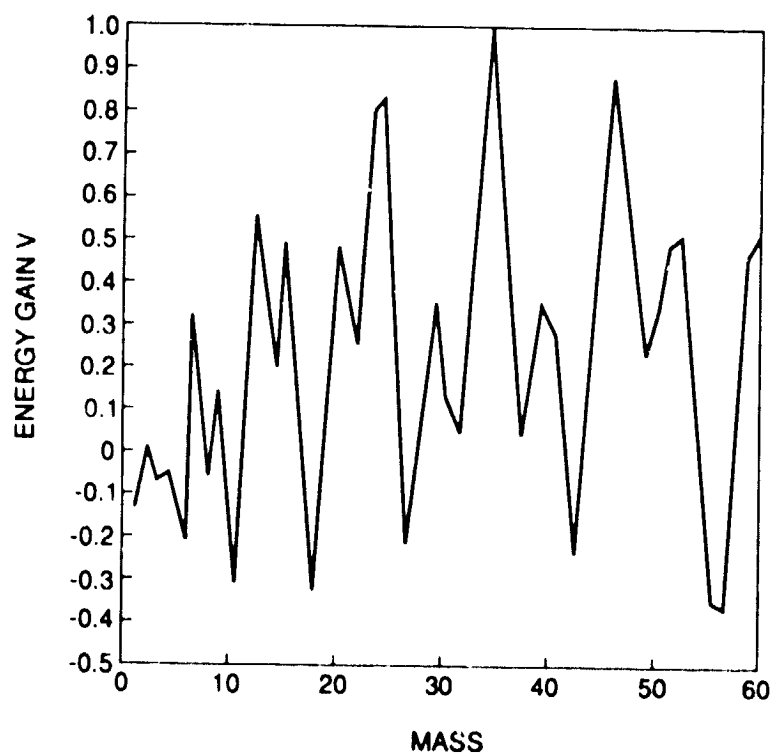


Figure 5. Standard mass spectrometer energy gain versus mass for designed phase of entry.

this type of mass spectrometer. Even though only one ion with the proper mass and phase can gain the maximum energy, there are others which can gain a large portion of it and these form the harmonics. Figure 6 is the same as Figure 5 except now the energy gained by an ion of specified mass is the maximum gained by that ion entering at its optimum phase. Notice that the main peaks do not change, indicating that the phase of entry allowing ions to gain the most energy is the one that the spectrometer has been designed for.

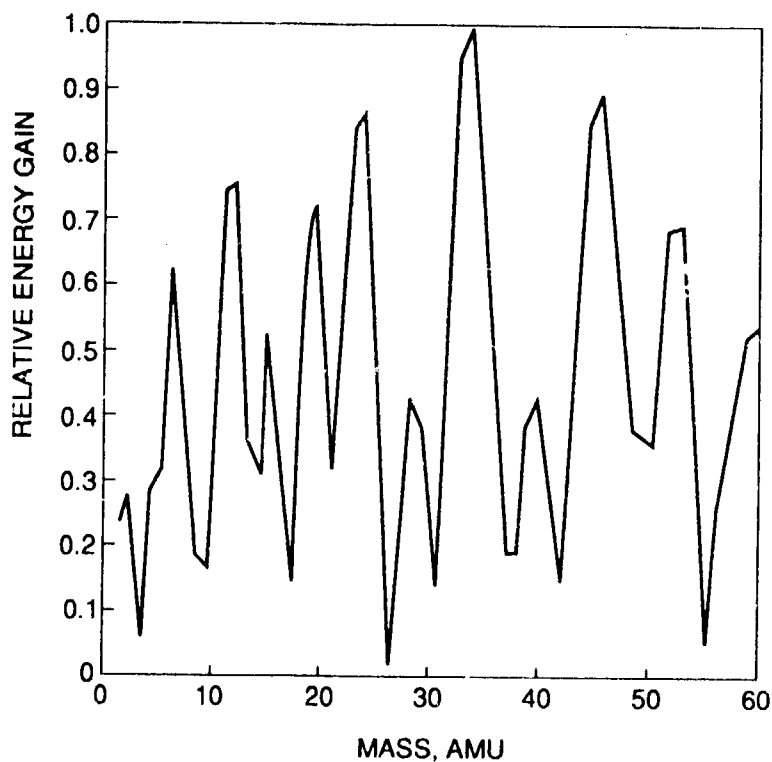


Figure 6. Mass spectrometer energy gain versus mass. (With energy gain for each mass being maximum for that ions optimum phase of entry.)

A Bennett mass spectrometer using square wave RF will be designed so that the ion selected to gain the maximum energy will traverse the Bennett stage width in one complete RF cycle. The square wave angular frequency at which the selected ion will gain maximum energy will be defined by,

$$\frac{s \omega}{v} = \pi$$

and therefore,

$$\omega = \frac{\pi}{s} \sqrt{\frac{2 e V_a}{m}}$$

As shown previously, other less massive ions with the same energy will be able to enter the stage at a different phase and gain the maximum energy while traversing a greater physical distance. Therefore, the question is: Will a three-stage, two-cycle Bennett mass spectrometer using square RF allow ions entering at different phases to gain maximum energy?

Equation (1) gives the electric field between grids one and two for a Bennett mass spectrometer using a sine-wave RF. A square-wave RF can be written using a Fourier series,

$$f(x) = \frac{4}{\pi} \sum_{n=1, \text{odd}}^n (-1)^{n+1} \frac{\sin [n(x+\delta)]}{n} \quad (4)$$

The number of terms in the Fourier series will establish the "cleanliness" of the square wave and the sensitivity to imperfect square wave shape can be assessed. The energy equation for an ion moving across a single stage for this case can be written as,

$$W = \frac{4 v V_{\text{RF}}}{s \pi} \left[ \int_0^{s/v} \sum_{n=1, \text{odd}}^n \frac{\sin (n\omega t + n\delta)}{n} dt - \int_{s/v}^{2s/v} \sum_{n=1, \text{odd}}^n \frac{\sin (n\omega t + n\delta)}{n} dt \right] \quad (5)$$

Since the functions are everywhere continuous and the summation represents a string of individual terms, the integral can be performed term by term and the summation sign brought outside the integral. Therefore, with

$$\sum_{n=1, \text{odd}}^n \equiv \sum_n$$

the energy gain analogous to equation (3) is,

$$W = \frac{2 v V_{\text{RF}}}{\pi s \omega} \sum_n \frac{(-1)^{n+1}}{n^2} \left[ \cos (n\delta) - 2 \cos \left( \frac{n s \omega}{v} + n\delta \right) + \cos \left( \frac{2 n s \omega}{v} + n\delta \right) \right. \\ \left. + \cos \left( \frac{(2s + D_1) n \omega}{v} + n\delta \right) - 2 \cos \left( \frac{(3s + D_1) n \omega}{v} + n\delta \right) \right]$$

(6)  
(Continued)

$$\begin{aligned}
& + \cos \left( \frac{(4s + D_1) n\omega}{v} + n\delta \right) + \cos \left( \frac{(4s + D_1 + D_2) n\omega}{v} + n\delta \right) \\
& - 2 \cos \left( \frac{(5s + D_1 + D_2) n\omega}{v} + n\delta \right) + \cos \left( \frac{(6s + D_1 + D_2) n\omega}{v} + n\delta \right) \Big] .
\end{aligned}
\tag{6}$$

(Concluded)

The maximum energy will be obtained for the ion of interest when it travels the distance between the first and third grids of a stage in one RF cycle. Therefore, the optimum phase of entry is zero. The field-free drift regions length must be an integral number of RF cycles and, therefore, equal to  $2N s$ . Figure 7 is the same as Figure 5 in that it represents the energy gain for a three-stage two-cycle Bennett type mass spectrometer except for the use of the square RF. As in Figure 5, the single phase of entry is for the maximum energy gain of the selected mass ion. It is similar to Figure 5 and the harmonics are low enough that they can be subdued. Figure 8 is analogous to Figure 6. Figure 8 is for the square-wave Bennett mass spectrometer and the energy gained by a specified mass ion is that gained by the ion entering with the optimum phase for maximum energy gain. Notice that the curves in Figures 7 and 8 are much different since the square wave allows more phases to obtain an optimum energy. Still, the three-stage, two-cycle Bennett spectrometer provides sufficient selection of phases so that only the selected ion with zero phase gains the maximum energy. The shape of the peaks are more triangular and pointed. This shape difference compared to the sine wave Bennett will change the relationship of sensitivity and resolution to the retarding potential.

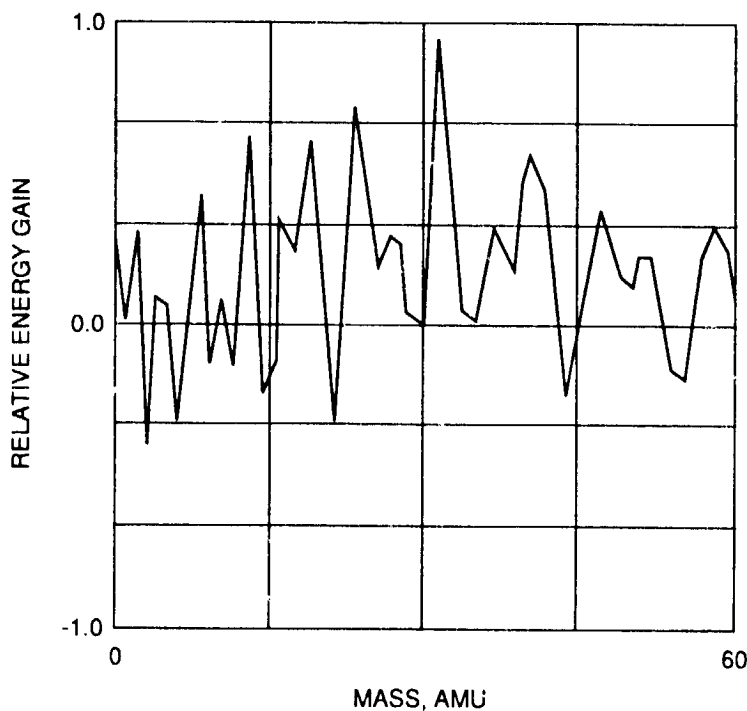


Figure 7. Square wave RF Bennett mass spectrometer energy gain versus mass. (For zero phase of entry.)



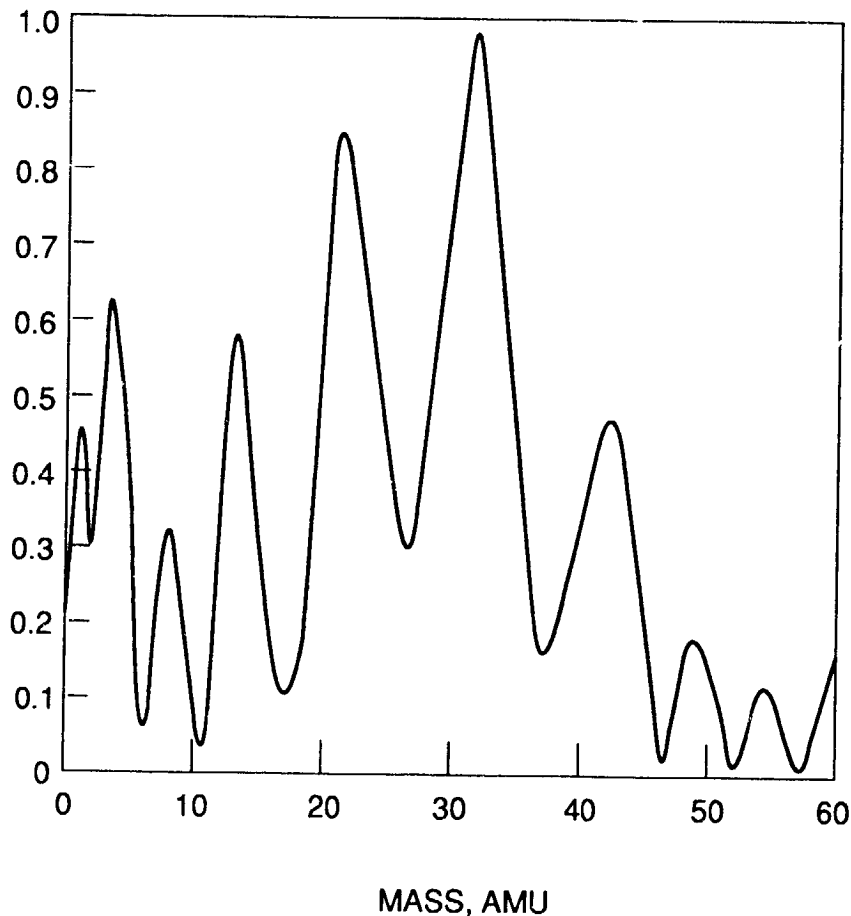


Figure 8. Square-wave RF Bennett mass spectrometer energy gain. (Energy gain for each mass being maximum for that ion's optimum phase of entry.)

### New Approaches

If an RF mass spectrometer system can be developed with fewer stages and drift regions, then it will be more compact, simpler, and have a greater sensitivity due to the greater physical transmission of ions to the collector. Attempts were made to find such a mass spectrometer. Several approaches were found which fit the criteria above. Instead of nine grids as in a three-stage Bennett, approaches which used five, six, or seven grids were found. The problem with most of them is harmonics. These new approaches may be useful if the researcher decides to live with harmonics. They will occur at known positions and can be separated. The spectra from radioactive materials and optical spectra must often be separated. Therefore, these approaches are described in Appendix A and the energy gain equations for them are given.

A couple of the approaches examined held more promise at controlling the harmonics than others and they will be discussed here. One of these approaches did not use a totally field-free region. As shown in Figure 9, it looks similar to the three-stage Bennett except that the third grid of the first two stages is the first grid of the next stage. What is normally the field-free drift region is not field free but the

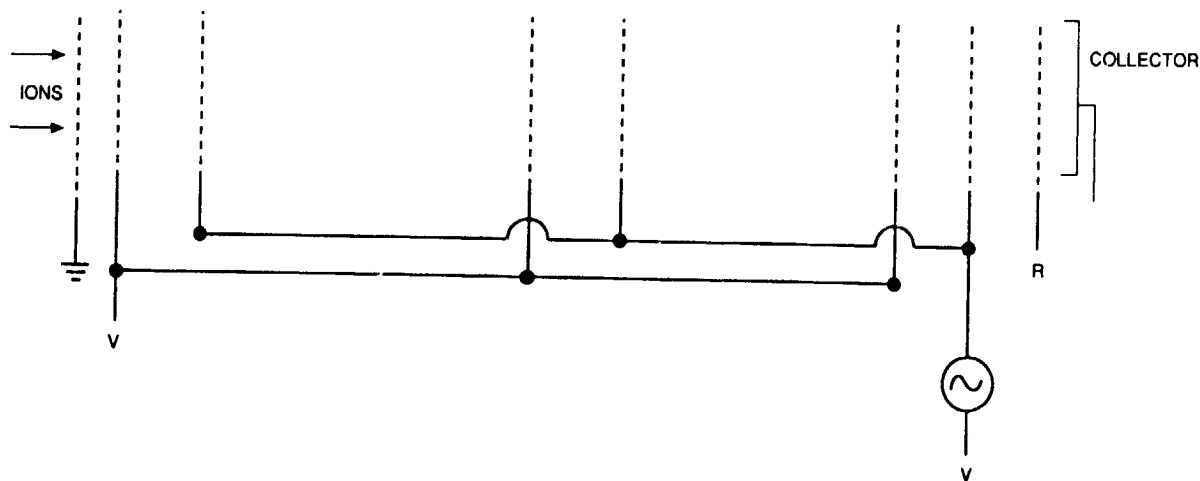


Figure 9. Diagram illustrating single acceleration mass spectrometer with quasi field-free drift.

ions see several RF cycles while traversing it, and the electric field is much weaker since the same potential difference is applied over a greater distance. The energy gain equation becomes,

$$\begin{aligned}
 W = v \left\{ - \frac{V_{RF}}{s\omega} \left[ \cos \left( \frac{s\omega}{v} + \delta \right) - \cos \delta + \cos \left( \frac{\omega(2s + D_1)}{v} + \delta \right) \right. \right. \\
 - \cos \left( \frac{(D_1 + s)\omega}{v} + \delta \right) + \cos \left( \frac{(3s + D_1 + D_2)\omega}{v} + \delta \right) \\
 - \cos \left( \frac{(2s + D_1 + D_2)\omega}{v} + \delta \right) - \cos \left( \frac{(4s + D_1 + D_2)\omega}{v} + \delta \right) \\
 \left. \left. + \cos \left( \frac{(3s + D_1 + D_2)\omega}{v} + \delta \right) \right] + \frac{V_{RF}}{\omega D_1} \left[ \cos \left( \frac{(D_1 + s)\omega}{v} + \delta \right) \right. \right. \\
 - \cos \left( \frac{\omega s}{v} + \delta \right) \left. \left. + \frac{V_{RF}}{\omega D_2} \left[ \cos \left( \frac{(2s + D_1 + D_2)\omega}{v} + \delta \right) \right. \right. \right. \\
 \left. \left. - \cos \left( \frac{(2s + D_1)\omega}{v} + \delta \right) \right] \right] \right\} . \tag{7}
 \end{aligned}$$

The ions gain most of their energy on the same one-half cycle of the RF. If the quasi-drift regions allow too many RF cycles then the harmonics are large. However, if the drift regions are a few cycles, the harmonics are similar to the standard Bennett.

These few RF cycles limit the resolution that can be obtained with this approach and the harmonics remain sufficiently small. Figure 10 indicates the maximum energy gained by each ion at its optimum phase.

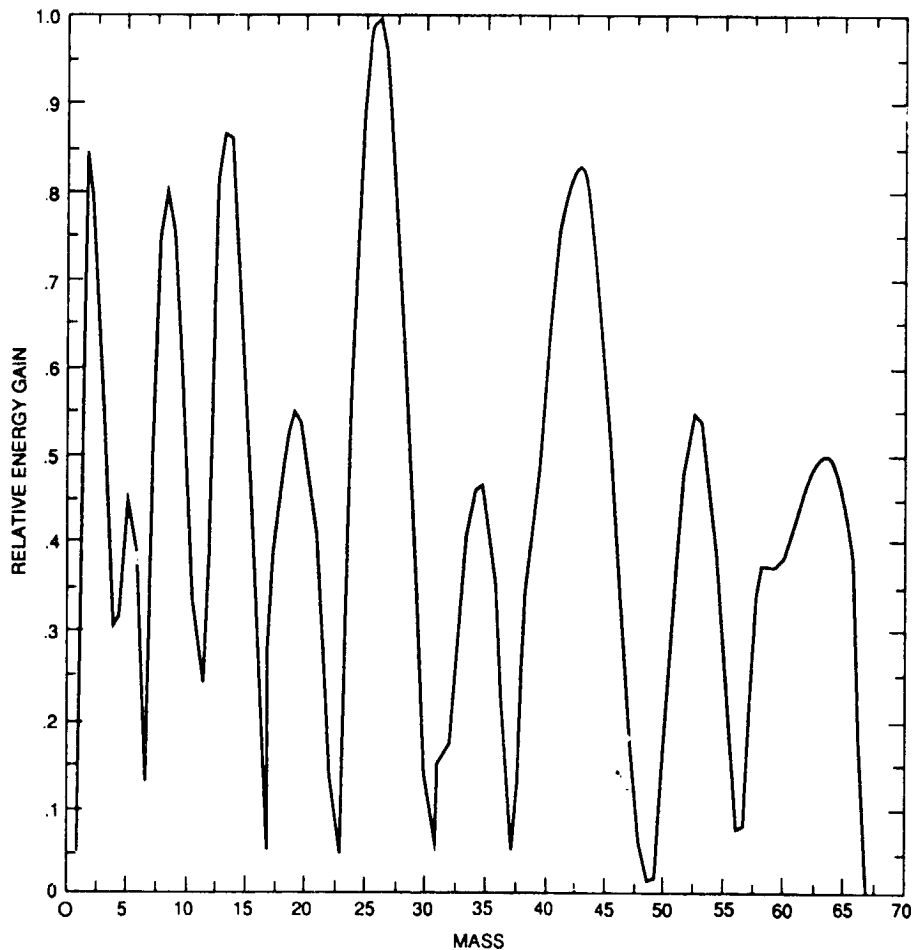


Figure 10. Energy gain curve. (Approach identified in Fig. 9.)

Another approach which has some merit is termed a hybrid mass spectrometer. This is because it is composed of a standard Bennett type stage with square-wave RF followed immediately by a stage as described by Henson, except that a sine wave is applied to it. The schematic approach is shown in Figure 11. Using only square-wave or sine-wave RF does not allow suppression of the harmonics. The sharpness of the energy gain curve for the single Bennett stage with square RF provides an increase in resolution as compared with the use of sine RF. Square-wave RF on the split stage allows ions of different phases to gain energy, such that the harmonics near the primary peak are very high. The application of sine wave to the split stage does a better job of selecting those phases which gain high energy. Therefore, the combined use of square- and sine-wave RF in this manner provided the best suppression of harmonics, second to the standard Bennett approach. The independent setting of the square- and sine-wave amplitude allows some tuning for maximum harmonic suppression. The hybrid concept uses six grids and one drift compared to the

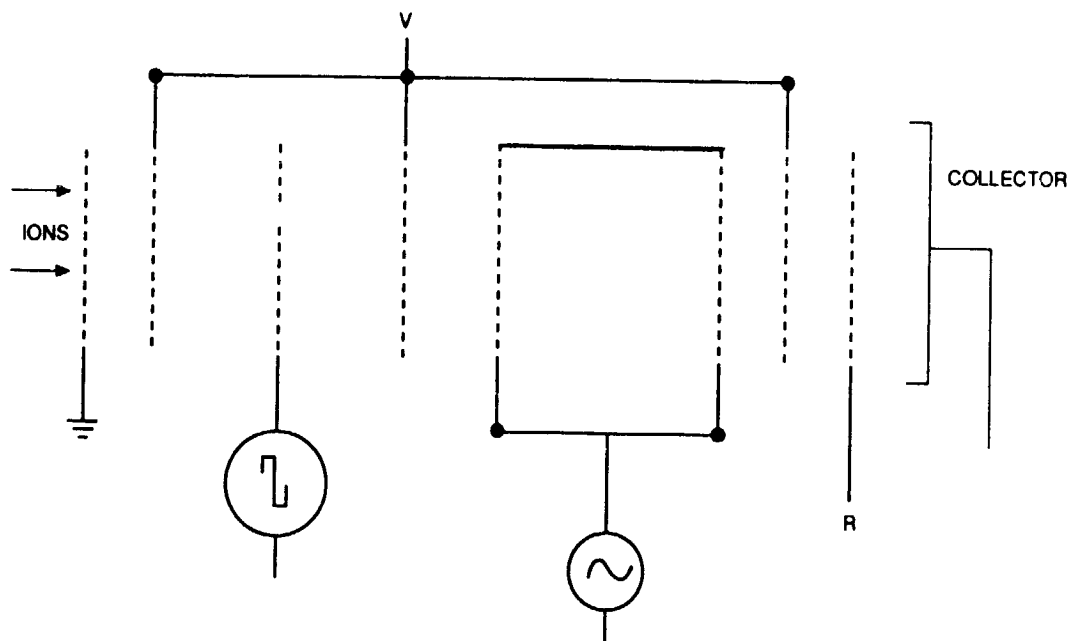


Figure 11. Diagram indicating hybrid Bennett approach.

Bennett nine grids and two drifts. Therefore, it is more compact and transmissive, but higher potentials must be used to suppress the harmonics. The energy gain expression for the hybrid concept is,

$$\begin{aligned}
 W = 2 v \frac{V_{RF}}{\pi s \omega} \sum_n \left\{ \frac{(-1)^{n+1}}{n^2} \left[ \cos(n \delta) - 2 \cos \left( n \omega \frac{s}{v} + n \delta \right) \right. \right. \\
 + \left. \left. \cos \left( 2 n \omega \frac{s}{v} + n \delta \right) \right] + v \frac{V_{sin}}{2 s_{sin}} \left[ \cos \left( 2 \omega \frac{s}{v} + \delta \right) \right. \right. \\
 - \left. \left. \cos \left( \omega \frac{2 s + s_{sin}}{v} + \delta \right) - \cos \left( \omega \frac{2 s + s_{sin} + D}{v} + \delta \right) \right. \right. \\
 \left. \left. + \cos \left( \omega \frac{2 s + 2 s_{sin} + D}{v} + \delta \right) \right] \right\} \quad (8)
 \end{aligned}$$

where  $D = (2.695 N - 2) s_{sin}$ .

Since both square- and sine-wave RF are used in this approach, the grid separations will be different. The same frequency of RF for both must be used. For a square wave, the maximum energy is gained by transit of a half stage in half an RF period. For the sine wave, the relation  $s_{sin}/v = 2.33$  must be satisfied. Therefore, if  $s$  here is the grid separation in a square-wave stage, the grid separation for the sine-wave portion,  $s_{sin}$ , is given by,  $s_{sin} = 0.74 s$ .

Figure 12 shows the energy gain for a hybrid system with the amplitude of the sine wave being 50 percent greater than the square wave. The energy gain by each mass in Figure 12 is also the maximum for that ions optimum phase.

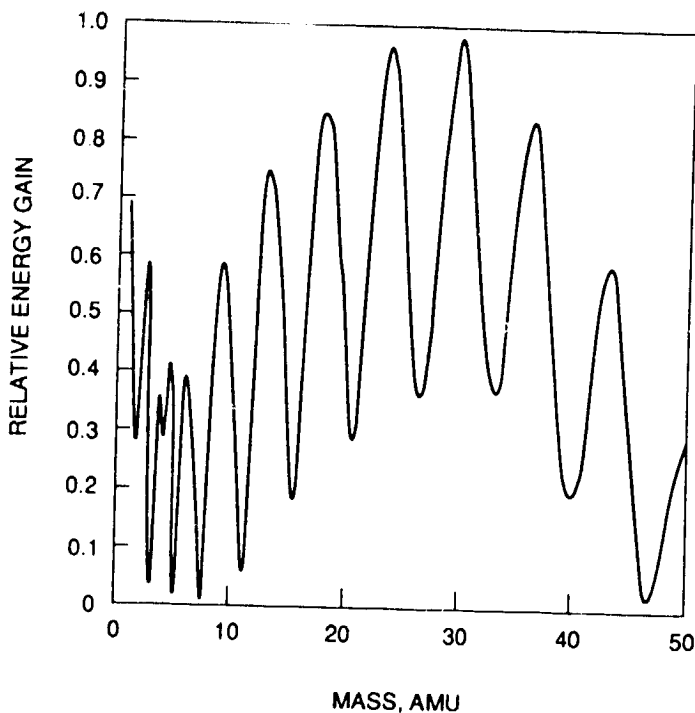


Figure 12. Energy gain curve for hybrid Bennett. (The relative gain is shown as a function of mass. The energy gained for each mass is the maximum for that mass's optimum phase of entry. For 30 eV energy gain the primary peak and first harmonic separation is approximately 1 eV.)

### EXPERIMENTAL INVESTIGATION

In order to examine the standard Bennett and other RF mass spectrometer approaches, the necessary laboratory apparatus was assembled as indicated in Figure 13. An electron bombardment ion source was used to produce accelerated beams of ions which were directed into the mass spectrometer. The mass spectrometer was designed so that the wire mesh grids were easily moveable and various configurations could be established. The wire mesh used was electroformed nickel, 70 by 70 lines per inch, and a physical transmission of 90 percent. The grids were configured on the outside so that the mass spectrometer unit was also used as a retarding potential analyzer (RPA). Figure 14 shows a typical RPA curve obtained. A second curve illustrates the RPA curve obtained when one Bennett stage is active. Some of the ions are accelerated to higher energies and some, if their mass and phase are wrong, lose energy. Of course, the energy gain by the desired ions is what allows the mass spectrometer to function.

Figure 15 gives the current as a function of the accelerating potential which gives the ions their velocity entering the Bennett stages. The variation in accelerating potential provides for mass selection. The retarding potential is small so that all

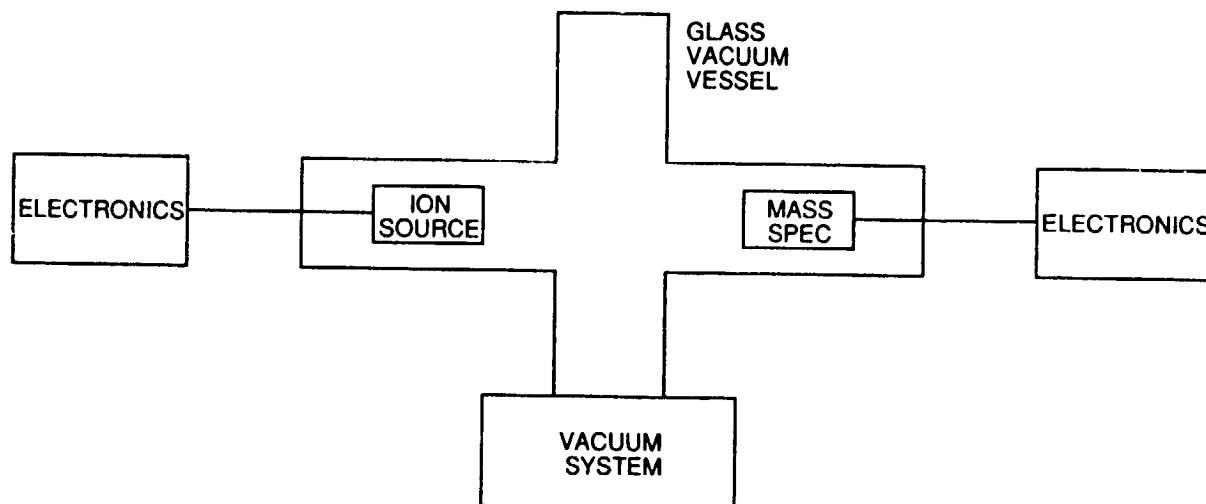


Figure 13. Experimental arrangement.

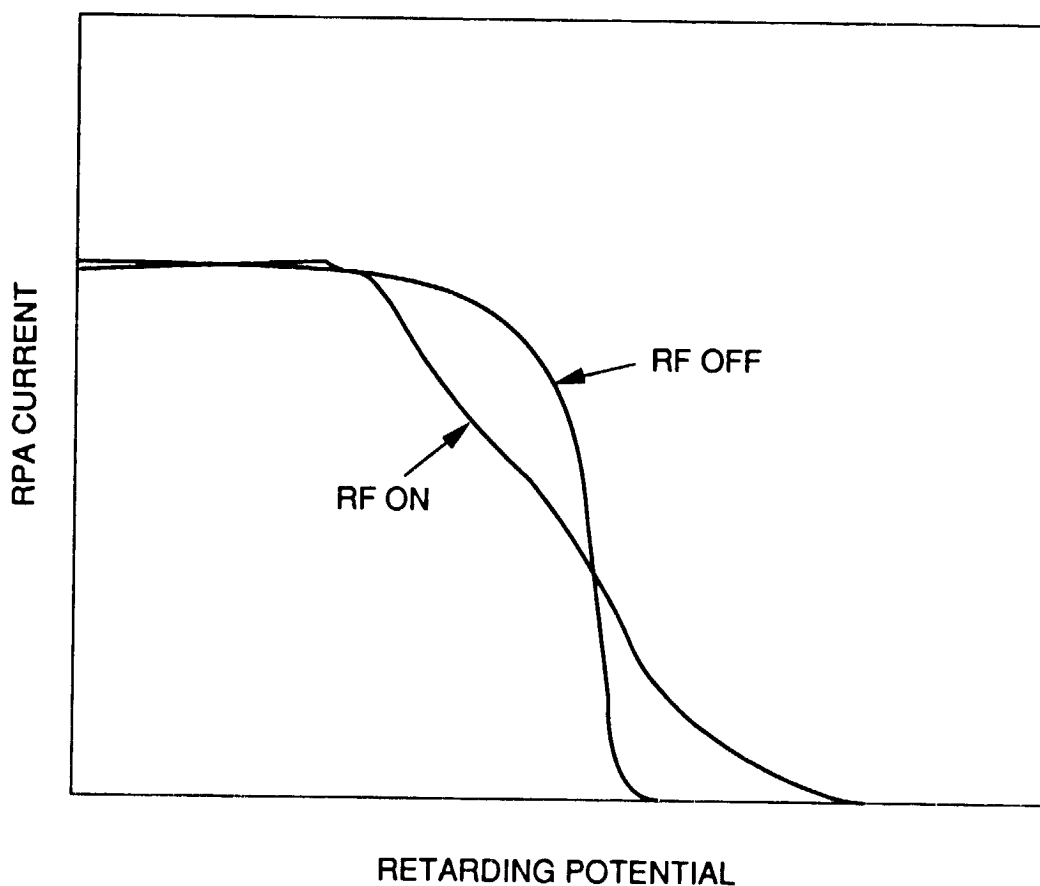


Figure 14. RPA curve with Bennett stage RF on and off. (With the RF off and the grids connected for RPA only, the typical RPA curve of the ions is obtained. With the RF on the Bennett stage some of the ions will gain energy and some will lose energy as indicated.)

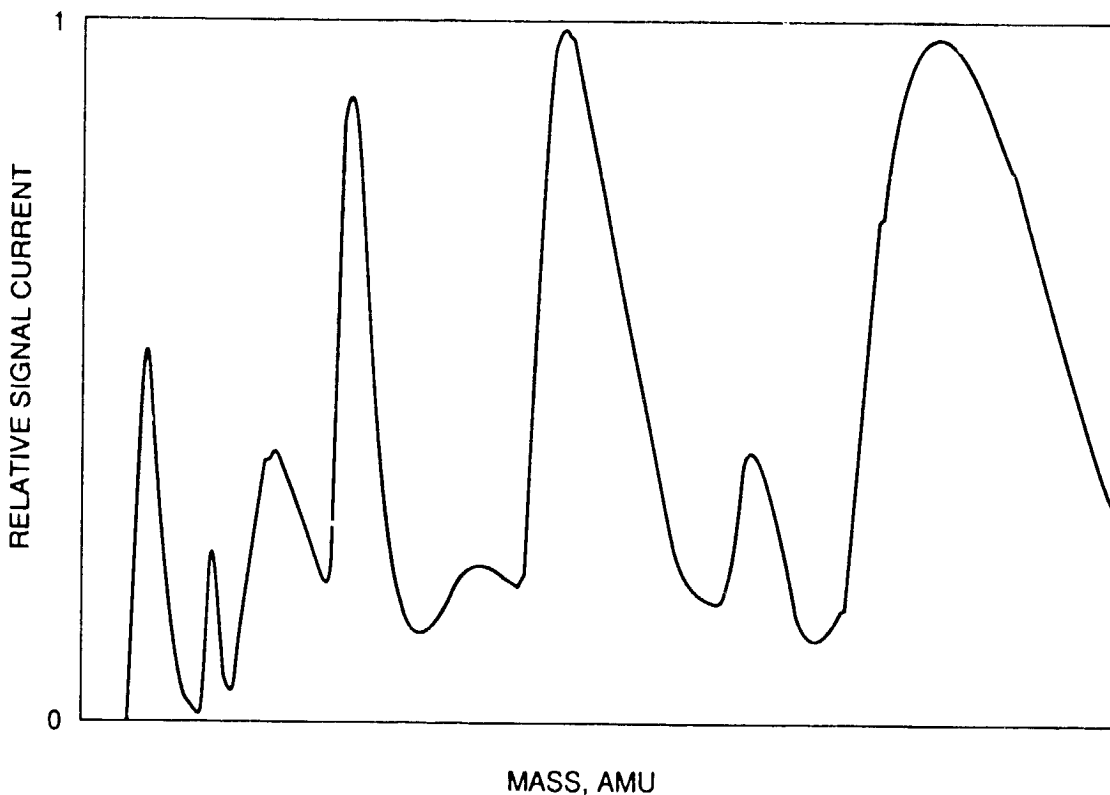


Figure 15. Experimental data showing primary and harmonic for a standard Bennett mass spectrometer.

harmonics show up. It can be seen that the curve fits the calculated curve in Figure 6. Figure 16 is part of the spectrum of air, and the molecular oxygen and nitrogen are clearly resolved. In general, the harmonic peaks were difficult to remove completely. As shown in Figure 17, there were extraneous peaks in the vacuum system used. Some of these peaks fell exactly on the harmonic peaks. Therefore, some of the residual peaks observed may not be totally due to hard-to-remove harmonics but background. High amplitudes (30 V peak-to-peak) are required so that clean, single peaks are obtained from the Bennett mass spectrometer [2,3].

The approach with the quasi field-free drift described earlier was examined experimentally. It was clear that the  $N_2$  and  $O_2$  peaks were clearly resolved and fell in exactly the calculated position. Some of the harmonic peaks, which should not have been large, according to the calculations, were extremely difficult to retard out. It was observed that, unlike the standard Bennett configuration, when the grids were joined into the RPA configurations, a clean RPA curve was not obtained. Since what was the field-free region now has a wall with an insulating surface, some surface charging may be taking place. If this is so, some means to prevent this may allow for more satisfactory operation.

The hybrid mass spectrometer approach outlined above was also examined. It was clear, as shown in Figure 18, that the harmonic peaks were evident. The configuration was such that the number of cycles which should have taken place in the drift tube during the ion transit was 12. It can be observed that at a different accelerating potential the ion transited the drift in descending integer cycles, producing harmonics. The experimental apparatus used did not allow application of sufficiently high RF amplitudes to retard the harmonics.

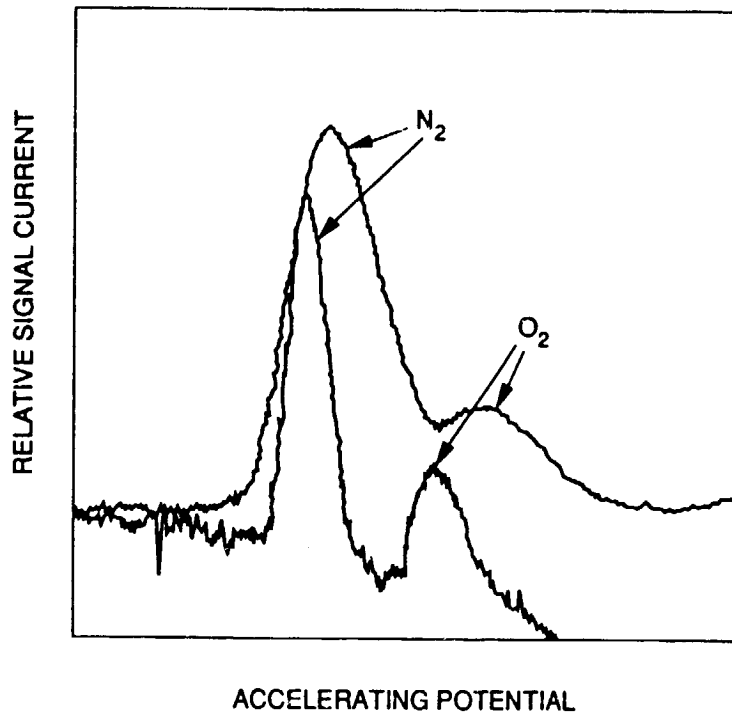


Figure 16. Experimental data of Bennett mass spectrometer. (The ion source is operating on air and the resulting molecular nitrogen and oxygen peaks are obtained. The more resolved data curve utilized a higher retarding potential to vary the resolution.)

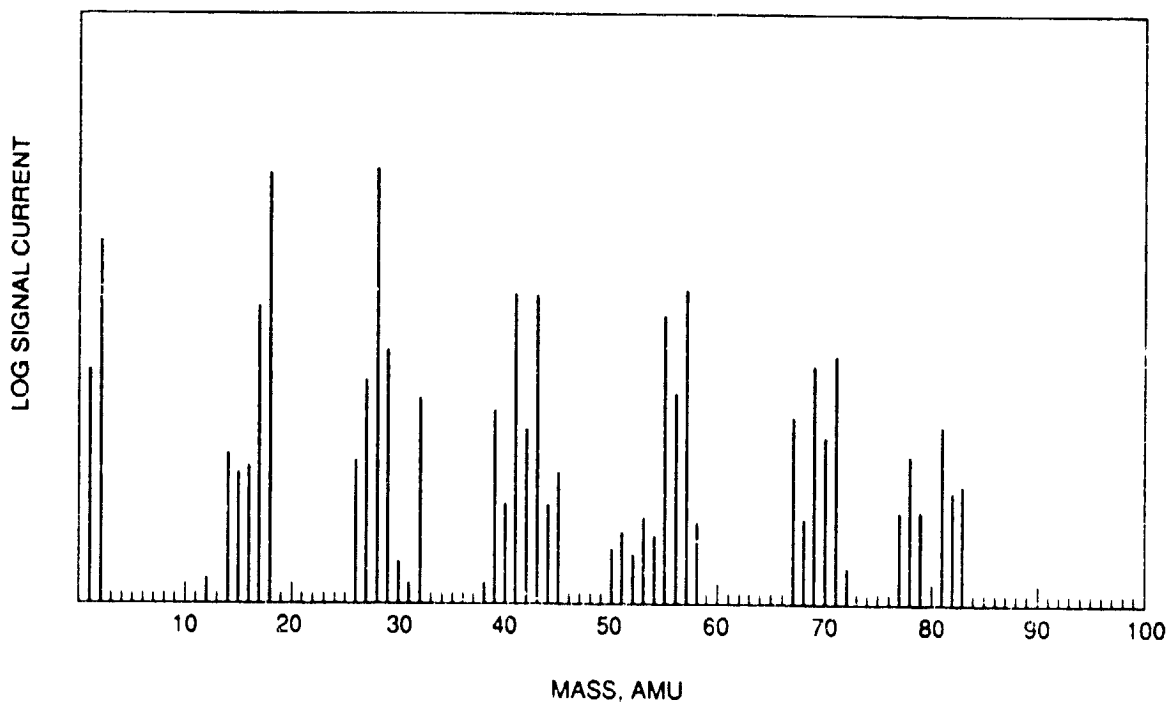


Figure 17. Vacuum system background.



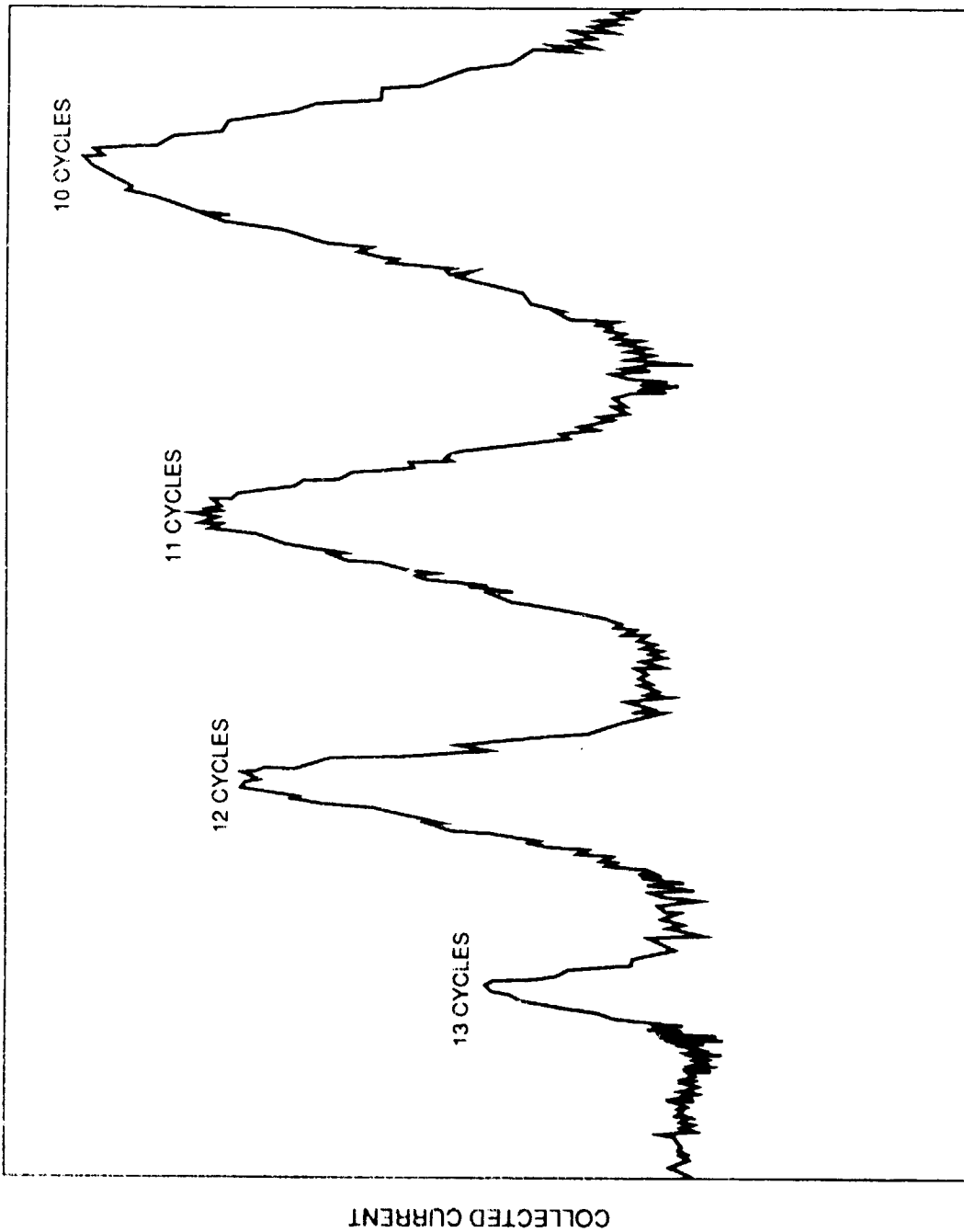


Figure 18. Data indicating integral cycle transmission of ions in the hybrid approach. (In this data square-wave RF is used on the standard Bennett stage and the split stage. The mass spectrometer was set for 12 RF cycles for the ion transit of the split stage. At higher accelerating potentials the ions transit with fewer integral RF cycles.)

The primary and harmonic peaks were observed to have a triangular shape as compared to the more rounded peaks when sine RF is used in the standard Bennett, as calculated.

The fine wire mesh of the grids is used to form a plane having a known potential. The 70-by-70 wire mesh provided a high physical transmission, and the closeness of the wires still provided a potential between wires which was sufficiently close to the potential applied to the wire. In order to increase the physical transmission through a number of grids, wire mesh of 70-by-7 was specially constructed. The small potential variation between grids will be slightly different from the square grid case. The closeness of the wires in the one axis still provides sufficient potential penetration into the gap. At the same time, the added 5 percent increase in physical transmission can provide substantial increase in throughput when up to 12 grids must be transited.

### SUMMARY

The standard Bennett mass spectrometer has long been used both in the laboratory and in space. An examination of modifications, short-cuts, and other RF approaches indicates that the standard Bennett or a Bennett using square wave RF probably provides the best approach. Other approaches were examined which were more compact and used fewer grids. However, the problem of harmonics is evident in all. It is necessary to have sufficient stages and drift sections to limit the combinations of ions and phases which can go through and gain all of the maximum available energy to one. Some of the approaches described in the literature reported to use the increased resolution and energy gain offered by the square wave RF. However, as indicated in this paper, ions of many different phases can enter and gain the maximum amount of available energy. The sawtooth will provide increasingly greater energy to faster ions that transverse it when it is near its maximum amplitude. The square wave can offer increased energy gain and resolution, but enough stages and drift regions must be included in the design so that the harmonics are sufficiently suppressed.

The quasi field-free drift approach offers a system with fewer grids and low harmonics but the resolution is seriously restricted. The hybrid approach described in this report is not unlike a two stage, one cycle Bennett mass spectrometer in performance. It is simpler and more compact than the standard three stage Bennett, but it is very difficult to prevent the harmonic peaks from showing up.

Some of the approaches which were tried had fewer grids than the standard Bennett but had the two drift regions for ion separation. However, harmonics were more of a problem still than with the standard Bennett configuration. This is because a split stage was used. The fact that there is a drift gap in a single stage allows for more harmonics. Faster ions can traverse the gap in fewer integral RF periods and, therefore, still gain maximum energy.

If one is willing to live with harmonics, some of the approaches given in the body of this report and in the Appendix may be useful. In most cases the harmonics appear close to the primary peak which will make identification of harmonic peaks simpler.

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## APPENDIX

In an effort to find a mass spectrometer which offers the desired resolution, sensitivity, and minimum harmonics with a reduced number of grids and drift regions, many approaches, which appeared feasible, were examined analytically. Because the harmonics continued to exist in all of these approaches, and this was undesirable, no further examination of these concepts was undertaken. It did not seem worthwhile to include this work in the body of the paper, but for completeness and for those who may be interested in pursuing some of these same concepts, they are briefly described in this appendix and the energy gain equation is given. In the descriptions of these approaches, it is always assumed that there exists an upstream grounded grid such that the grids with set potential define the ion energy entering the system.

A pulsed approach with a single Bennett stage was considered. Initially, the first four grids in this arrangement are at the same set accelerating potential. The first three grids are close together and the region between the third and fourth grids is a field-free drift region. A pulsed potential is applied to the first and second grid. The ions between them will exit and see an increased electric field between the second and third grids while the pulse is on. The grids following grid four make up a standard Bennett stage, retarding grid, and collector. Therefore, the pulse of ions with additional energy will separate in the drift region and only those ions with the selected phase will enter the standard Bennett so as to gain maximum energy. If the time separation between pulses is sufficient, then this approach will work. However, it was observed that if the grids are pulsed frequently, then the slower and faster ions from different pulses can be at the same position in the drift region and harmonics still exist since the single Bennett stage has a low resolution. If the pulse rate is reduced, then the duty cycle is low and the throughput is not attractive.

An approach similar to the hybrid Bennett spectrometer was examined. The first three grids make up a Bennett stage with square-wave RF applied. The separation between the third and fourth grids and the fifth and sixth grids is very small. If the phase of the square RF and sine RF (applied to the fourth and fifth grids) is correct, the ions passing the split stage will see a near dc field which coincides with the maximum potential of the sine-wave RF. For a drift region which must be an integral amount plus a half and for a grid separation for the split stage of 0.2 of the square-wave stage, the energy gain equation is

$$\begin{aligned}
 W = & 2 v \frac{V_{RF}}{\pi s \omega} \sum_n \left\{ \frac{(-1)^{n+1}}{n^2} \left[ \cos(n \delta) - 2 \cos\left(n \omega \frac{s}{v} + n \delta\right) + \cos\left(2 n \omega \frac{s}{v} + n \delta\right) \right] \right\} \\
 & + v_i \frac{V_{sin}}{2 s_{sin} \omega} \left[ \cos\left(2 \omega \frac{s}{v} + \delta + \alpha\right) - \cos\left(\omega \frac{2 s + s_{sin}}{v} + \delta + \alpha\right) \right. \\
 & \left. - \cos\left(\omega \frac{2 s + s_{sin} + D}{v} + \delta + \alpha\right) + \cos\left(\omega \frac{2 s + 2 s_{sin} + D}{v} + \delta + \alpha\right) \right] \quad (A-1)
 \end{aligned}$$

with

$$\alpha = \frac{72}{180} \pi \quad , \quad \beta = \frac{36}{180} \pi \quad , \quad \text{and} \quad D = 2 N s + \frac{\beta}{\pi} s - 0.4 s \quad .$$

For a total energy gain of 36 eV, the nearest harmonic is approximately 0.5 eV lower in energy. The other harmonics maximum energy reduces quickly.

An approach using essentially two split stages was examined. The first grid is at a set potential. The second and third grid have an applied square RF and the distance between them is a drift region. The third grid and fourth grid are spaced the same as between grids one and two. The fourth and fifth grids also have an applied square RF and a drift region between them. The two square RF potentials that are applied to the pair of grids is 180 deg out of phase. The energy gain equation is,

$$\begin{aligned} W = 2 v \left( \frac{V_{RF}}{\pi s \omega} \right) \sum_n \left\{ \frac{(-1)^{n+1}}{n^2} \left[ \cos(n \delta) - \cos \left( n \frac{s \omega}{v} + n \delta \right) + 2 \cos \left( n \omega \frac{s + D_1}{v} \right. \right. \right. \\ \left. \left. \left. + n \delta \right) - 2 \cos \left( n \omega \frac{s + D_1}{v} + n \delta \right) + \cos \left( n \omega \frac{2s + D_1 + D_2}{v} + n \delta \right) \right. \right. \\ \left. \left. \left. - \cos \left( n \omega \frac{3s + D_1 + D_2}{v} + n \delta \right) \right] \right\} \quad . \end{aligned} \quad (A-2)$$

For the condition described which leads to equation (A-2), except with sine-wave RF, the energy gain equation is,

$$\begin{aligned} W = v \left( \frac{V_{RF}}{2 s \omega} \right) \left[ \cos(\delta) - \cos \left( \frac{s \omega}{v} + \delta \right) + 2 \cos \left( \omega \frac{2s + D_1}{v} + \delta \right) - 2 \cos \left( \omega \frac{s + D_1}{v} \right. \right. \\ \left. \left. + \delta \right) + \cos \left( \omega \frac{2s + D_1 + D_2}{v} + \delta \right) - \cos \left( \omega \frac{3s + D_1 + D_2}{v} + \delta \right) \right] \quad . \end{aligned} \quad (A-3)$$

For a hybrid Bennett with square-wave RF applied to both the standard stage and the split stage, the energy gain equation is,

$$\begin{aligned}
W = 4 v \frac{V_{RF}}{s \pi \omega} \sum_n \frac{1}{n^2} & \left[ \cos (n \delta) - 2 \cos \left( n s \frac{\omega}{v} + n \delta \right) + \cos \left( 2 n s \frac{\omega}{v} + n \delta \right) \right. \\
& + \cos \left( (2 s + D_1) n \frac{\omega}{v} + n \delta \right) - 2 \cos \left( (3 s + D_1) n \frac{\omega}{v} + n \delta \right) \\
& + \cos \left( (4 s + D_1) n \frac{\omega}{v} + n \delta \right) + \cos \left( (4 s + D_1 + D_2) n \frac{\omega}{v} + n \delta \right) \\
& \left. - 2 \cos \left( (5 s + D_1 + D_2) n \frac{\omega}{v} + n \delta \right) + \cos \left( (6 s + D_1 + D_2) n \frac{\omega}{v} + n \delta \right) \right] . \quad (A-4)
\end{aligned}$$

The following two approaches tried to reduce the number of grids by merging the RF and sine-wave energy gain in the same region. Instead of having grids at fixed potentials to provide the electric field between them and the grids with RF applied, one RF was applied to a grid and another RF was applied to the adjacent grid. The phase was selected for maximum energy gain by selected ions. Some of the harmonics still gain nearly the maximum available energy.

In one of these approaches, the first grid is at a set potential. The second and fifth grid have a square-wave RF applied at the same phase. A sine-wave RF is applied to grids three and four. An ion traversing these grids sees a square wave RF between grids one and two, both the square- and sine-wave RF between grids two and three, a drift region between grids three and four, again both square- and sine-wave RF between grids four and five, and the square-wave RF between grids five and six. The energy gain equation for this case is,

$$\begin{aligned}
W = 2 v \frac{V_{RF}}{\pi s \omega} \sum_n & \left\{ \frac{(-1)^{n+1}}{n^2} \left[ \cos (n \delta) - \left( 1 + \frac{s}{s_{\sin}} \right) \cos \left( n \omega \frac{s}{v} + n \delta \right) \right. \right. \\
& + \left( \frac{s}{s_{\sin}} \right) \cos \left( n \omega \frac{s + s_{\sin}}{v} + n \delta \right) - \left( 1 + \frac{s}{s_{\sin}} \right) \cos \left( n \omega \frac{s + 2 s_{\sin} + D}{v} + n \delta \right) \\
& \left. \left. + \left( \frac{s}{s_{\sin}} \right) \cos \left( n \omega \frac{s + s_{\sin} + D}{v} + n \delta \right) + \cos \left( n \omega \frac{2 (s + s_{\sin}) + D}{v} + n \delta \right) \right] \right\} \\
& + v \frac{V_{\sin}}{2 s_{\sin}} \left[ - \cos \left( \omega \frac{s}{v} + \delta \right) + \cos \left( \omega \frac{s + s_{\sin}}{v} + \delta \right) - \cos \left( \omega \frac{s + 2 s_{\sin} + D}{v} + \delta \right) \right. \\
& \left. + \cos \left( \omega \frac{s + s_{\sin} + D}{v} + \delta \right) \right] \quad (A-5)
\end{aligned}$$

A similar approach has a set potential on the first grid and a square RF on the second grid. A sine RF is applied to the third and fourth grid and the fifth grid is at a set potential. An ion sees the square RF potentials between the first and second and second and third grids. The sine RF field is experienced also between the second and third grids with only the sine field seen by the ion between the fourth and fifth grids. The energy gain equation is,

$$\begin{aligned}
 W = 2 v \frac{V_{RF}}{\pi s \omega} \sum_n \left\{ \frac{(-1)^{n+1}}{n^2} \left[ \cos(n \delta) - \left(1 + \frac{s}{s_{\sin}}\right) \cos\left(n \omega \frac{s}{v} + n \delta\right) \right. \right. \\
 \left. \left. + \left(\frac{s}{s_{\sin}}\right) \cos\left(n \omega \frac{s + s_{\sin}}{v} + n \delta\right) \right] \right\} + v \frac{V_{\sin}}{2 \omega s_{\sin}} \left[ - \cos\left(\omega \frac{s}{v} + \delta\right) \right. \\
 \left. + \cos\left(\omega \frac{s + s_{\sin}}{v} + \delta\right) - \cos\left(\omega \frac{s + 2 s_{\sin} + D}{v} + \delta\right) + \cos\left(\omega \frac{s + s_{\sin} + D}{v} + \delta\right) \right]
 \end{aligned}
 \tag{A-6}$$

In order to have an additional drift region to aid in ion separation, the following approach was considered. A Bennett stage with square-wave RF applied is followed by a drift region which is then followed by a split stage with a sine RF applied to it. The energy gain equation for this case is given by

$$\begin{aligned}
 W = 2 v \frac{V_{RF}}{\pi s \omega} \sum_n \left\{ \frac{(-1)^{n+1}}{n^2} \left[ \cos(n \delta) - 2 \cos\left(n \omega \frac{s}{v} + n \delta\right) + \cos\left(2 n \omega \frac{s}{v} + n \delta\right) \right] \right\} \\
 + v \frac{V_{\sin}}{2 s_{\sin}} \left[ \cos\left(\omega \frac{2 s + D_1}{v} + \delta\right) - \cos\left(\omega \frac{2 s + s_{\sin} + D_1}{v} + \delta\right) \right. \\
 \left. - \cos\left(\omega \frac{2 s + s_{\sin} + D_1 + D_2}{v} + \delta\right) + \cos\left(\omega \frac{2 s + 2 s_{\sin} + D_1 + D_2}{v} + \delta\right) \right].
 \end{aligned}
 \tag{A-7}$$


Numerous other approaches were considered. However, most all of them are variations of those already reported, some with various combinations of sine, square, and even other types of wave equations. In general, these variations produced minor differences in performance and there is no need to report all the variations here.

APPROVAL

REEXAMINATION OF RADIOFREQUENCY MASS SPECTROMETERS  
Center Director's Discretionary Fund Final Report

By M. R. Carruth, Jr.

The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

  
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