V. ELECTRONIC INSTRUMENTATION*

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A. STATUS OF RESEARCH

During the past quarter, theoretical studies of the effects of power-supply variations on mass-spectrometer resolution have been completed. A new project has been initiated to investigate scanning techniques for detection systems employing a definite number of detectors. Reports in both areas appear below. Also, ultrahigh stability power-supply circuits are being tested for possible application in the mass-spectrometer system.

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B. PRECISION POWER SUPPLY

A power supply is being designed and built for use in the electric sector of a mass spectrometer. The goal is a voltage source variable from 380 V to 420 V with ripple and

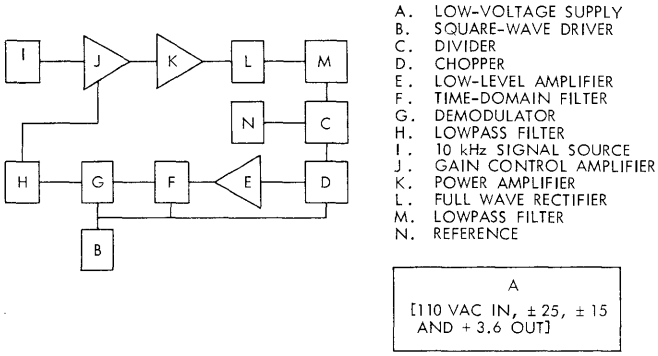

Fig. V-1. Precision power supply.

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noise no greater than one part in 10^7 and stable within one part in 10^6 per day. Figure V-1 shows a proposed block diagram.

The following sections have been breadboarded: chopper, low-level amplifier, time-domain filter, demodulator, 10-kHz signal source square-wave drive and low-voltage power supply.

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C. EFFECTS OF POWER-SUPPLY VARIATIONS ON THE RESOLUTION OF A DOUBLE-FOCUSSING MASS SPECTROMETER

The concern of our group at this time is the stabilization of the resolution of the CEC 21-110 mass spectrometer and the subsequent design of an electronic interface between the instrument and a high-speed digital computer. These plans have been described in previous reports.[1,2] Part of the program includes the introduction of ultrastable power supplies for the instrument's electric and magnetic sectors. This report concerns the results of theoretical research on the extent to which power supply variations degrade the instrument's resolution. This degradation has been determined experimentally, and also by means of a computer simulation of the instrument previously described.[3]

This report gives a general description of the instrument and a discussion of the double-focussing principle. The trajectories of single ions are considered in detail for no power-supply variations, and the limiting resolution and mass dispersion are given. The dispersion is shown to result mainly from velocity variations of ions entering the accelerator sector, and the theory of distributions reported earlier is used to obtain the shape of an ion beam in the exit plane for a Maxwell-Boltzmann distribution of initial ion velocities.

Two types of power-supply variations are considered: random variations, and 60-cycle hum. Both types of variation in accelerator voltage are shown to have a negligible effect compared with that caused by variations in the electric sector voltage and magnetic sector field strength, because of the double-focussing nature of the instrument. The random variations in the electric and magnetic sectors is shown to introduce additional dispersion in the ion trajectories which tends to degrade the resolution by a fixed amount. It is shown that the 60-cycle hum in both sectors can produce a double-peak mass spectrum from a single-peak spectrum, and in general will have the cumulative effect of widening the average extent of the ion beam.

1. Description of the Machine

The CEC 21-110 mass spectrometer is of the Mattauch-Herzog variety and its geometry is shown schematically in Fig. V-2. Its function is to discriminate ions with regard

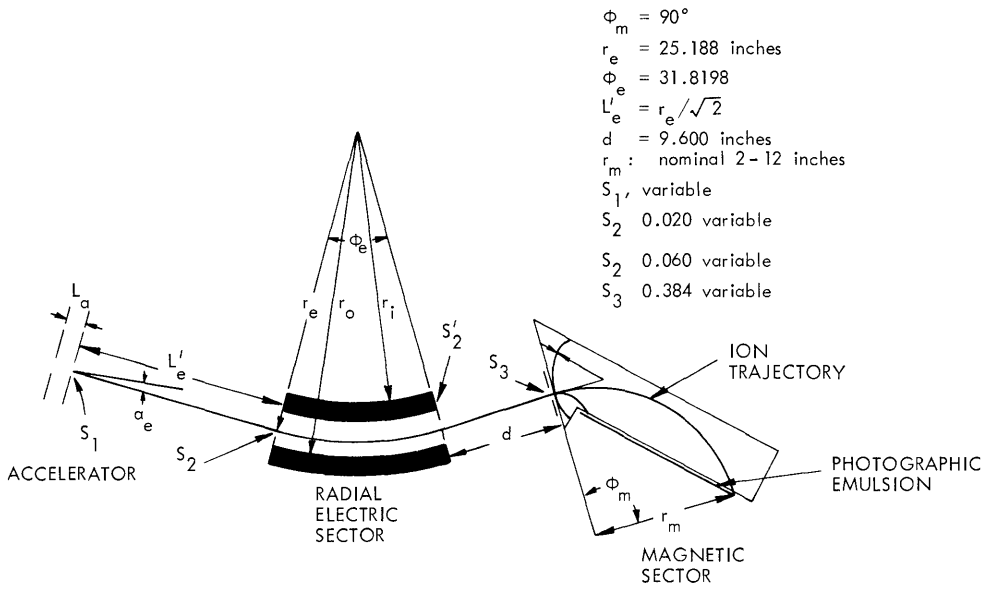

Fig. V-2. Mattauch-Herzog geometry.

to their mass-to-charge ratio. It consists of an evacuated chamber containing an accelerator, radial electric sector, and magnetic sector. Its operation is as follows: Ions accelerated to a potential of 8-10 kV enter the instrument at S_1, pass through the two sectors and are recorded on a flat photographic emulsion. Ideally, the position at which an ion strikes the emulsion is a function only of its mass-to-charge ratio. Practically, the position at which an ion of given mass-to-charge ratio strikes the emulsion is a function of its initial position and velocity upon entering the accelerator. The effect of variations in initial position and velocity on the distribution of ions on the emulsion has been considered previously for a general instrument.

The Mattauch-Herzog instrument has been designed so that the effects of first-order variations in the magnitude and direction of the velocity of ions leaving the accelerator are eliminated.[4] This "double-focussing" feature is achieved for the dimensions shown and for a given ratio of electric sector potential to accelerator potential, 10:1 for the CEC 21-110. There is still a first-order effect caused by the fact that ions of a given mass-to-charge ratio may leave the accelerator at different points within the aperture of slit S_1. This variation in aperture position is the result of a random transverse velocity component of ions entering the accelerator. The details of the double-focussing scheme and of the trajectories and dispersions of ions will now be considered.

2. Dispersion with No Power Supply Variations

To understand the effects of power-supply variations on ion trajectories, it is necessary to consider in more detail the effects of mass dispersion, velocity dispersion,

and aperture dispersion. For reference, the trajectory of a dispersionless ion will be followed. Consider an initially stationary ion of mass M_o and charge Q_o which is accelerated through a potential V_a and leaves the accelerator from the center of slit S_1, traveling perpendicular to the aperture of slit S_1.

The energy of the ion is given by

$$\frac{1}{2} M_o V_o^2 = Q_o V_a, \tag{1}$$

where V_o is the speed. The ion enters the electric sector at a zero potential radius. The zero potential radius, r_e, is obtained by exciting the outer field plate, r_o, by a potential $+V_e/2$ and the inner field plate, r_i, by a potential $-V_e/2$ and by positioning the two plates so that

$$r_e = \sqrt{r_o r_i}. \tag{2}$$

The potential difference between the plates, V_e, is chosen so that the trajectory of the ions in the radial electric sector is a circle of radius r_i.

$$V_e = 2V_a \ln (r_o/r_i). \tag{3}$$

The ion emerges from the electric sector with the initial energy given by Eq. 1 and continues in a straight line to the magnetic sector. In the magnetic sector the ion again describes a circle whose radius r_b is given by

$$r_b = \frac{Q_o B_o}{M_o V_o}, \tag{4}$$

where B_o is the magnetic flux diversity. The ion emerges from the magnetic sector at a position X_f measured along the magnetic sector exit plane given by

$$X_f = \sqrt{2}\ r_b. \tag{5}$$

Now consider the effects of dispersion on Eq. 5. Suppose that an ion of $M_o(1+\gamma)$ has an initial position and velocity at the entrance to the accelerator so that it emerges from slit S_1 with an angle α_e, a deviation from the center of S_1 in the plane of S_1 of $r_e\rho_o$, and a speed of $V_o(1+\beta)$.

It can be shown that to first order in γ, α_e, ρ_o, and β Eq. 5 becomes

$$X_f = \sqrt{2}\ r_b \left(1 + \frac{\gamma}{2} - \rho_o\right). \tag{6}$$

Equation 6 indicates that the angular dispersion α_e and speed dispersion β at S_1 do

not affect the exit position X_f to first order. It also indicates that in addition to mass dispersion, γ, there is an aperture dispersion, ρ_o, caused by ions emerging from different points in the aperture of slit S_1.

The mass dispersion is given by

$$\Delta X_M = \frac{\sqrt{2}}{2} r_b \left(\frac{\Delta M}{M_o}\right), \tag{7}$$

which corresponds to 350 μ-2100 μ for a 1% mass difference. The maximum aperture dispersion is given by

$$\Delta X_A = \sqrt{2}\, \frac{r_b}{r_e} S_1, \tag{8}$$

where S_1 is the slit width. The theoretical limiting resolution is defined as that ratio of $M/\Delta M$ for which the dispersion caused by the finite slit width is equal to the mass dispersion:

$$\text{Resolution} = \frac{M}{\Delta M} = \frac{r_e}{2S_1}. \tag{9}$$

For a typical slit width of 2.5 μ, the resolution is 125,000. Resolutions of 30,000 have been achieved in the actual instrument. The discrepancy between the limiting resolution and the experimental resolution is the result of many factors, among which are machining errors, fringing errors, mechanical vibration, thermal expansion, and power-supply variations.

The aperture dispersion ρ_o can be related to the random variation in transverse velocity at the entrance to the accelerator. If we assume that the accelerator has length ℓ_a, an ion of mass M_o having an initial transverse velocity V_x and an initial displacement of Δ will emerge from S_1 at a position given by

$$\rho_o r_e = \Delta + \frac{2V_x}{V_o} \ell_a, \tag{10}$$

where V_o is the exit speed. The theoretical shape of the beam in the exit plane of the instrument can be obtained to first order from the probability distribution of V_x. For example, if V_x has a probability distribution $f(V_x)$ and the ions enter the accelerator from a point source (Δ=0), the distribution of ions in the plane of S_1 is proportional to $f\left(\frac{\rho_o r_e V_o}{2\ell_a}\right)$ and the distribution of ions at the exit plane is proportional to

$f\left(\frac{r_e V_o}{2\ell_a}\frac{(X_f-\sqrt{2}\,r_b)}{\sqrt{2}\,r_b}\right)$. To first order the effect of the finite slit width is to truncate F at the limits $X - \sqrt{2}\,r_b = \pm\sqrt{2}\,\frac{r_b S_1}{2r_e}$.

Therefore, if $f(V_x)$ is a Gaussian of the form

$$f(V_x) \sim \exp\left(-\frac{1}{2}\frac{M_o V_x^2}{kT}\right) \tag{11}$$

the probability distribution of ions or ion beam shape in the exit plane to first order is proportional to

$$f \sim \exp\left[-\frac{1}{2}\frac{MV_o^2}{kT}\left(\frac{1}{4}\frac{r_e^2}{\ell_a^2}\right)\left(\frac{X_f - \sqrt{2}\,r_b}{\sqrt{2}\,r_b}\right)^2\right]$$

$$\frac{|X_f - \sqrt{2}\,r_b|}{\sqrt{2}\,r_b} < \frac{S_1}{2r_e}. \tag{12}$$

For typical values of the parameters, f is essentially constant over a range of X_f which amounts to a fraction of a slit width. The details of converting single ion trajectories into ion distributions have been reported previously.[3]

3. Dispersion Caused by Random Power Supply Variations

We have found that the dispersion of ions in a double-focussing mass spectrometer is independent of the magnitude and direction of the ion velocity at the exit slit of the accelerator to first order, and depends only on the position of ions in the aperture of the exit slit of the accelerator. These results are valid if the dimensions of the instrument are specified exactly as in Fig. V-2 and if the voltage supplied to the accelerator and electric sector are related by Eq. 3. Any deviations from the dimensions indicated by Eq. 3 will result in dispersion. A small variation in accelerator potential will not result in any first-order dispersion, since it causes a first-order variation in ion speed at slit S_1, and the instrument is insensitive to these variations, as shown in Eq. 6.

A small variation in electric sector potential and magnetic sector field will effect the exit point of an ion to first order and this dispersion will now be considered.

Suppose the electric sector potential varies because of small error voltages added in on each plate, so that the outer plate has a potential $\frac{V_e}{2}(1+v_o)$ and the inner plate has a potential $\frac{V_e}{2}(1+v_i)$, where v_o and v_i are small quantities. Suppose that v_o and v_i do not change appreciably during the time that the ion is in the electric sector, and also

that the magnetic field varies so that $B = B_o(1+b)$, where b is a small quantity that does not change appreciably during the time that the ion is in the magnetic sector. The times involved are approximately 2.5 μsec for the electric sector and 2.5 μsec for the magnetic sector for an accelerator potential of 10 kV and a singly charged ion of mass of 100 AMU. To first order the exit position of the ion is then given by

$$X_f = \sqrt{2}\ r_b \left(1 + \frac{\gamma}{2} - \rho_o - b - \frac{1}{2}(v_o+v_i) - \frac{1}{2}(v_o-v_i)\ \ln\left(\frac{r_o}{r_i}\right)\right), \tag{13}$$

where γ, ρ_o, r_b, r_o, and r_i have been defined previously. Equation 13 indicates that a 1% variation in each electric sector supply is equivalent to a 1% mass change, and a 1% variation in magnetic field is equivalent to a 2% mass change. It is assumed that b, v_o, v_i change randomly from ion to ion as independent random variables with zero mean and standard deviation σ, the rms deviation of X_f is given by

$$\text{rms} = \sqrt{\langle X_f^2\rangle - \langle X_f^2\rangle} = \sigma\sqrt{\frac{3}{2} + \frac{1}{2}\ln\left(\frac{r_o}{r_i}\right)} \tag{14}$$

and the resolution of the instrument is given by

$$\frac{M}{\Delta M} = \frac{1}{2\left(\frac{S_1}{r_e} + \sigma\sqrt{\frac{3}{2} + \frac{1}{2}\ln\left(\frac{r_o}{r_i}\right)}\right)}. \tag{15}$$

Therefore, in order to achieve a resolution of 30,000, the power-supply variations must be held to 0.001% for a 2.5-μ slit. Equation 15 has been plotted in Fig. V-3. The

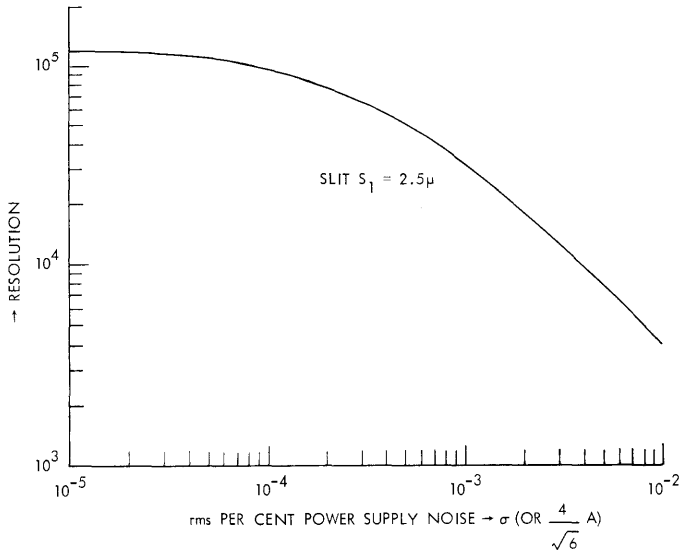

Fig. V-3.

Degradation of resolution of CEC 21-110 mass spectrometer with random power-supply error.

results indicate that if the power supplies are tuned up so that double focussing is achieved, random noise in each power supply can seriously degrade the resolution. The calculations are only valid under the assumptions that the fields do not change appreciably while the ion is passing through them and that the noise is random.

4. Dispersion with 60-cycle Hum

The effects of 60-cycle hum on the resolution of the mass spectrometer will now be considered. The transit time of the ion through the system is short compared with the 60-cycle period: 10 μsec as compared with 1/60 of a second, so that the fields can be assumed constant for an individual ion.

Therefore Eq. 13 is still valid, except that b, v_o, v_i will each be a sinusoid with a radian frequency of 120π and a different phase angle. Equation 13 can be written for the N^{th} ion in terms of the following variables:

$$\begin{aligned} b &= \underline{b}_o \cos (120\pi t_N + \phi_o) \\ v_o &= \underline{v}_o \cos (120\pi t_N + \phi_1) \\ v_i &= \underline{v}_i \cos (120\pi t_N + \phi_2) \end{aligned} \tag{16}$$

where t_N is the time in seconds at which the N^{th} ion leaves slit S_1, $\underline{b}_o$, $\underline{v}_o$, $\underline{v}_i$ are amplitudes of the respective signals, and ϕ_o, ϕ_1, ϕ_2 are constant phase angles. Equation 13 can now be written in the form

$$X_f = \sqrt{2}\, r_b \left(1 + \frac{\gamma}{2} - \rho_o + A \cos (120\pi t_N + \phi)\right), \tag{17}$$

where

$$A = \left| b\, e^{j\phi_o} + \frac{\underline{v}_o}{2}\left(1 + \ln\left(\frac{r_o}{r_i}\right)\right) e^{j\phi_1} + \frac{\underline{v}_i}{2}\left(1 - \ln\left(\frac{r_o}{r_i}\right)\right) e^{j\phi_2} \right|, \tag{18}$$

and ϕ is some constant phase.

It will be assumed that ions emerge from slit S_1 at a constant rate and have the same mass. Suppose A = 0 but, because of random variations in ρ_o, there is a probability distribution of ions in the exit plane given by $f(X_f)$. If A is nonzero, then the probability distribution of those ions emerging from slit S_1 at times t_o, $t_o + \frac{1}{60}$, $t_o + \frac{2}{60}$, etc. will be proportional to

$$f(X_f - \sqrt{2}\, r_b A \cos (120\pi t_o + \phi)). \tag{19}$$

Therefore, on the average, the probability distribution of ions in the exit plane $\left\langle f(X_f) \right\rangle$

will be given by the average of Eq. 19 over t_o.

$$\left\langle f(X_f) \right\rangle = \frac{1}{2T} \int_{-T}^{T} f(X_f - \sqrt{2}\ r_b A \cos(120\pi t_o + \phi))\ dt_o. \tag{20}$$

Define the new variable

$$X_f = \sqrt{2}\ r_b A \cos(120\pi t_o + \phi). \tag{21}$$

Equation (20) becomes an average over 240T half-cycles of the cosine wave plus an amount ϵ

$$\left\langle f(X_f) \right\rangle = \frac{1}{2T}\left[\frac{240T}{120\pi} \int_{-\sqrt{2}\ r_b A}^{+\sqrt{2}\ r_b A} \frac{f(X_f - x)\ dx}{\sqrt{2r_b^2A^2 - x^2}} + \epsilon\right]. \tag{22}$$

As T approaches infinity, ϵ remains finite, and $\left\langle f(X_f) \right\rangle$ approaches the limit

$$\left\langle f(X_f) \right\rangle = \frac{1}{\pi} \int_{-\sqrt{2}\ r_b A}^{+\sqrt{2}\ r_b A} \frac{f(X_f - x)\ dx}{\sqrt{2r_b^2A^2 - x^2}}. \tag{23}$$

Equation 23 expresses the average probability distribution of ions in the exit plane, with 60-cycle hum in the power supplies, in terms of the probability distribution with no hum, $f(X_f)$, and the total amplitude of the hum signal, A. Presumably $\left\langle f(X_f) \right\rangle$ is what appears on the photographic emulsion. Equation 23 can also be written

$$\left\langle f(X_f) \right\rangle = \frac{1}{\pi} \int_{X_f - \sqrt{2}\ r_b A}^{X_f + \sqrt{2}\ r_b A} \frac{f(x)\ dx}{\sqrt{2r_b^2A^2 - (x - X_f)^2}}, \tag{24}$$

which shows that $\left\langle f(X_f) \right\rangle$ will in general be broader in extent than $f(X_t)$. If f is of finite extent because of the finite slit width S_1, then the extent of $\left\langle f(X_f) \right\rangle$ is equal to $\sqrt{2}\,\frac{r_b S_e}{r_e} + 2\sqrt{2}\ r_b A$, and the resolution in the case of hum is then given by

$$\frac{M}{\Delta M} = \frac{1}{\frac{2S_1}{r_e} + 4A}. \tag{25}$$

The curve of Fig. V-3 applies to Eq. 24 with the horizontal axis labeled $\dfrac{4A}{\sqrt{6 + 2\ln\left(\frac{r_o}{r_i}\right)}}$.

It is important to observe that the distribution of ions produced in the presence of hum is equal to the "convolution" of the distribution of ions produced in the absence of hum with the function g given by

$$g = \frac{1}{\pi} \cdot \frac{1}{\sqrt{2r_b^2A^2 - x^2}}, \tag{26}$$

where g is the "impulse response" of a mass spectrometer with hum, which is peaked sharply at $x = \pm \sqrt{2}\, r_b A$, corresponding to the maximum deflections caused by the hum,

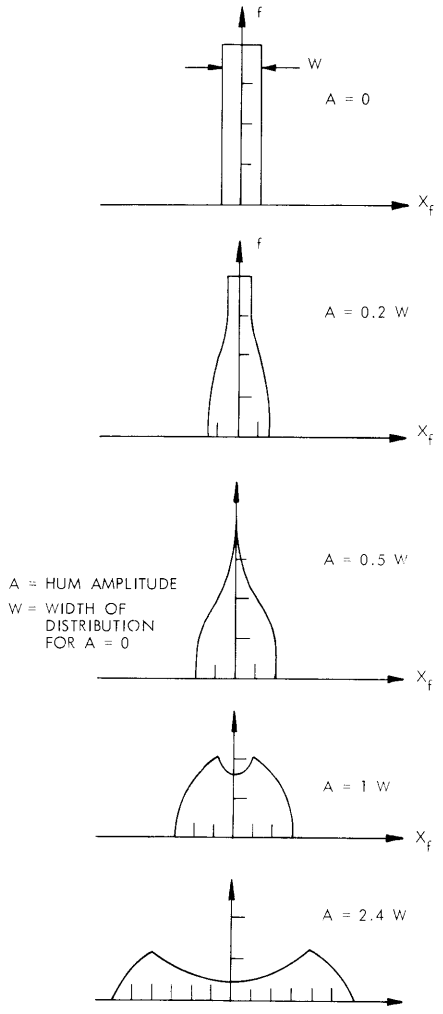

Fig. V-4.
Effect of hum on ion distribution.

because on the average the sine-wave hum signal spends most of its time near its maximum. Equation 25 indicates that the effect of hum on a single-peaked narrow distribution of ions is to produce a double-peaked distribution, and the effect of hum on a

single-peaked wide distribution is to produce an even wider distribution as shown in Fig. V-4. The terms "wide" and "narrow" are used with reference to the spatial extent of g.

5. Conclusion

This work indicates that power-supply variations of a random nature and also of a periodic nature can seriously affect the performance of a high-resolution double-focussing mass spectrometer. As a rule of thumb, the resolution will be halved when the percentage power-supply variation is equal to the reciprocal of the resolution. For example, an instrument with a theoretical resolution of 1 part in 60,000 will have an effective resolution of 1 part in 30,000 when the rms power-supply variation is 0.001%. These results were obtained from a first-order theory; higher order effects should reduce the resolution even more.

The random fluctuations will tend to broaden a single-peaked ion distribution. The 60-cycle hum will tend to broaden any distribution of ions and can produce a double-peaked distribution from a single-peaked distribution.

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References

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D. DETECTION SCHEMES FOR AUTOMATED MASS SPECTROMETERS

1. Introduction

An important effort of our group at this time is the development of an electronic interface between a high-resolution mass spectrometer and a high-speed digital computer. This interface would replace the present photographic scheme. The interface would have as inputs the distribution of ions in space and time along the focal plane of the spectrometer, and as outputs electrical signals from which the computer would determine the spatial distribution of ions to an accuracy equal to or greater than that of the present system. There are two interrelated problems associated with the interface

design: the choice of detectors, and the choice of a detection scheme. This report contains some preliminary results on the detection problems.

2. Finite Detection Schemes

The finite detection schemes under consideration comprise a finite number of ion detectors located at different points in the focal plane of the instrument. Each detector would provide an electrical output when an ion impinged upon its aperture. The maximum information available from each detector is the total ion current of charge striking it. To get information on ion currents at points between detectors, a scanning scheme would be needed; for example, the distribution of ion currents could be shifted by changing the magnetic field in the magnetic sector of the instrument. A possible sequence of events for the finite detection scheme would be to have the magnetic field held constant for some preset interval of time. The number of ions striking each detector during this interval would be counted and stored. The magnetic field would then be stepped to a new value for the same time interval and again the number of ions would be counted and stored. The procedure would be repeated until sufficient information were obtained to resolve the spectrum. The choice of magnetic field levels and counting interval would be a function of the number of detectors, aperture size of an individual detector, spacing between detectors, ion rate of generation, time that the ion spends in the magnetic field, and desired resolution. Much work must be done to determine the best choice of parameters, as well as the limitations on the scheme imposed by field transients, statistical fluctuations in the counts, errors in the placement of the detectors along the focal plane, and the cost of the detectors.

The choice of individual detectors is rather limited. Two possibilities are electron multiplier, and semiconductor devices. The electron multiplier produces a pulse each time an ion strikes its aperture. A single multidynode multiplier is built into commercially available spectrometers and is used for low-resolution scans. A study of the Bendix "Channeltron," a tiny electron multiplier is being made by N. T. Tin; present indications are that the "Channeltron" has a low ion detection efficiency and that it may be contaminated by heavy ions.

Two semiconductor devices that might be feasible are the field-effect transistor and the silicon diode. The FET would be used by letting ions deposit charge on the gate and controlling the conduction of current between source and drain. An array of FET's could be deposited on a substrate by integrated circuit techniques so that the drains are tied to a common wire. The sources could be scanned by an electron beam. The total drain current would be an indication of the accumulated charge on each FET. A similar array could be constructed with silicon diodes. The ion beams would bombard the diodes, and therefore vary their conductivity by producing hole electron pairs. The difficulties with the semiconductor detectors are ion contamination, shot noise, and size

limitations imposed by present integrated circuit technology.

3. Continuous Detection Schemes

The continuous detection scheme that is envisioned consists of a homogeneous surface that responds in some way to ion bombardment as a function of space and time and a scanner that reads off the effects of bombardment as an electrical signal. Examples of a continuous light detection method are the Vidicon and image orthicon tubes used in television cameras. A modified version of these tubes could be directly put into the focal plane of the spectrometer, provided that (a) an ion sensitive phosphor could be found to replace the light sensitive phosphor, (b) the resolution were maintained over the focal plane area (17 × 1/4 in.), and (c) the magnetic field of the instrument did not affect the electron trajectories in the tube. These three difficulties may be insurmountable with present technology. Furthermore, there is a possibility of phosphor deterioration with ion bombardment.

Another scheme might be to place a luminescent surface in the focal plane which would give off light at points where ions strike. This light could then be detected outside the spectrometer by a Vidicon or image orthicon. The resolution of this scheme is limited by the spot size on the luminescent surface. Commercially available tubes have a resolution of 5000 lines/inch, an order of magnitude too small for high-resolution spectrometry. Other semiconductor surfaces could be used in the continuous detection scheme such as field-sustained conductivity layers, but all of these may suffer from ion contamination. A thorough investigation of these schemes is being undertaken.

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