# III. ELECTRONIC INSTRUMENTATION*

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## A. RESOLUTION OF THE MASS SPECTROMETER

### 1. General Aims

In attempting to improve the resolution of the CEC 21-110 mass spectrometer, a study of the factors influencing the resolution has been undertaken. A theoretical study of the spatial distribution of ions in the exit focal plane as a function of the spatial and velocity distributions of ions in the input focal plane has been made with the aid of a computer-simulation of the actual instrument. The theory and computer program will be outlined in this report and some preliminary results will be given. The object of this study is to determine the beam shape in the exit focal plane so that correlation techniques can be used to resolve minute mass differences.

### 2. Theory of Distributions

In most general terms, a high-resolution mass spectrometer is an instrument that resolves ions of different masses by accelerating them through a combination of electric and magnetic fields. The fields are chosen so that ions of differing mass emerge from the fields at different locations in a focal plane where they may be detected by a photographic plate or electrometer tube. A perfect instrument would focus all ions of a given mass and charge at a single point, independently of the initial positions and velocities that the individual ions had on entering the fields. Unfortunately, practical instruments disperse ions of the same mass and charge in the exit focal plane according to their position and velocity in the input focal plane.

The CEC 21-110 mass spectrometer is of the double-focussing variety; it consists of an accelerator, radial electric field sector, and magnetic sector. The dimensions and field strengths have been specifically chosen by the manufacturer to minimize the

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dispersion of the exiting ions of a given mass. Slits located between the sectors also serve to minimize dispersion by effectively eliminating stray ions.

If the spectrometer is considered as a two-dimensional machine characterized by a linear input focal plane $x_i$ and a linear exit focal plane $x_e$, an ion of mass M and charge Q entering at $x_i$ with velocities perpendicular to the input focal plane $v_{zi}$ and parallel to the input focal plane $v_{xi}$ will appear in the exit focal plane at $x_e$. There is a relation between $x_e$ and $x_i$, $v_{xi}$, $v_{zi}$, M, Q which is a function of the instrument:

$$x_e = x_e(x_i, v_{xi}, v_{zi}, M, Q). \tag{1}$$

Consequently, if a burst of ions of differing masses, charges, and velocites is generated in the input plane, the distribution of ions in the exit plane can be obtained by solving Eq. 1 for each ion in the burst. Of course, this procedure is tedious by hand and hence a computer was employed to obtain a plot of distributions of ions in the exit focal plane as a function of the distribution of ions in the input focal plane. All parameters of the instrument were left adjustable so that the effects of changes in dimensions and field strengths could be studied theoretically. Before describing the computer program, it is instructive to examine the problem of relating the input and exit distributions from a statistical point of view.

It is assumed that the generation of ions in the input focal plane has statistical regularity so that the process is describable by a probability density function, f, which is a continuous function of the initial positions and velocities and a discrete function of the masses and charges; the masses must be integral multiples of the atomic mass unit and the charges integral multiples of the electronic charge. The number of particles entering the instrument of mass M, charge Q, with positions between $x_i$ and $x_i + dx_i$, velocities between $v_{xi}$ and $v_{xi} + dv_{xi}$, $v_{zi}$ and $v_{zi} + dv_{zi}$, where "d" denotes a differential element, is

$$dn_i = f(x_i, v_{xi}, v_{zi}, M, Q)\ dx_i dv_{xi} dv_{zi}. \tag{2}$$

These particles $dn_i$ appear in the exit focal plane at points governed by Eq. 1. The number of particles appearing between points $x_e$ and $x_e + dx_e$ in the exit focal plane are denoted by

$$dn_e = F(x_e)\ dx_e, \tag{3}$$

where F is the probability density function of ions in the exit focal plane, and is determined by integrating Eq. 2 over all particles exiting in the range $dx_e$ and then dividing the total by $dx_e$. This procedure is automatically accomplished in the computer program by means of a histogram subroutine. The mass spectrometer can be thought of as a device that maps a five-dimensional space onto a 1-dimensional line.

Mathematical relationship between F and f can be written as

$$\int_{x_e}^{x_e+dx_e} F(x_e)\, dx_e = \sum_{M} \sum_{Q} \iiint f(x_i, v_{xi}, v_{zi}, M, Q)\, dv_{xi} dv_{zi} dx_i \tag{4}$$

where the integration and summation extend over those particles that end up in the range $dx_e$. It is clear that f and F are related in a very complex manner. In the interest of demonstrating the analytic procedure, a burst of ions having the same initial position, mass, and charge will be assumed; hence, f and $x_e$ are independent of $x_i$, M, and Q. The relationship of Eq. 1 is then given by

$$x_e = x_e(v_{xi}, v_{zi}). \tag{5}$$

Equation 4 can then be simplified to the form

$$F(x_e) = \int \frac{ds\ f(v_{xi}, v_{zi})}{\left[\left(\frac{\partial x_e}{\partial v_{xi}}\right)^2 + \left(\frac{\partial x_e}{\partial v_{zi}}\right)^2\right]^{1/2}}, \tag{6}$$

where the integration is carried out along a line of constant $x_e$ in the $(v_{xi}, v_{zi})$-plane governed by Eq. 5. This result can be extended to the situation in which $x_e$ depends on any number of input variables in a continuous manner

$$F(x_e) = \iiiint \frac{dA\ f(v_{xi}, v_{zi}, x_i, M, Q)}{\left[\left(\frac{\partial x_e}{\partial v_{xi}}\right)^2 + \left(\frac{\partial x_e}{\partial v_{zi}}\right)^2 + \left(\frac{\partial x_e}{\partial x_i}\right)^2 + \left(\frac{\partial x_e}{\partial M}\right)^2 + \left(\frac{\partial x_e}{\partial Q}\right)^2\right]^{1/2}}, \tag{7}$$

where the integration has been carried out over a four dimensional hypersurface of constant $x_e$ in five-dimensional space, and f is assumed to be a delta function at the discrete mass and charge values in the input distribution.

In order to illustrate the effect of dispersion, a few simple examples will be considered: $v_x$ dispersion alone, $v_z$ dispersion alone, and $v_x$ and $v_z$ dispersion combined.

a. $v_x$ Dispersion Alone

Suppose that N particles with mass M enter the instrument with a Maxwellian distribution in $v_{xi}$ at temperature T and a constant velocity in the z direction, $v_{zo}$, from an infinitesimally narrow slit. f is given by

$$f = N\sqrt{\frac{M}{2\pi kT}}\exp\left(-\frac{mv_{xi}^2}{2kT}\right)\delta(v_{zi}-v_{zo}). \tag{8}$$

Suppose that the $v_x$ dispersion of the instrument is linear and given by

$$x_e = x_o + \alpha v_{xi}. \tag{9}$$

The distribution of particles in the exit focal plane is given by

$$F = N\sqrt{\frac{M}{2\pi kT\alpha^2}}\exp\left(-\frac{M(x_e-x_o)^2}{2kT\alpha^2}\right) \tag{10}$$

which is a Gaussian with a 1/e width of

$$W = 2\sqrt{\frac{2kT\alpha^2}{M}}. \tag{11}$$

b. $v_z$ Dispersion Alone

Suppose that N particles with mass M enter the instrument with a Maxwellian distribution in $v_z$ centered about $v_{zo}$ and with $v_{xi} = 0$ from an infinitesimally narrow slit. f is given by

$$f = N\sqrt{\frac{M}{2\pi kT}}\exp\left(-\frac{m(v_{zi}-v_{zo})^2}{2kT}\right)\delta(v_{xi}). \tag{12}$$

(The fact that particles with negative $v_{zi}$ do not enter the instrument is neglected, since $v_{zo}$ has been chosen sufficiently large so that their number is negligible.) Suppose, furthermore, that $v_z$ dispersion is linear and given by

$$x_e = \beta v_z. \tag{13}$$

The distribution of particles in the exit plane is given by

$$F = N\sqrt{\frac{M}{2\pi kT\beta^2}}\exp\left(-\frac{M}{2kT}\left(\frac{x_e}{\beta} - v_{zo}\right)^2\right) \tag{14}$$

which is also a Gaussian with a 1/e width of

$$W = 2\sqrt{\frac{2kT\beta^2}{M}}. \tag{15}$$

c. $v_x$ and $v_z$ Dispersion Combined

Suppose now that both dispersions are combined and that the initial distributions of $v_x$ and $v_z$ are combined. f is now given by the product of Eqs. 8 and 12:

$$f = N\left(\frac{M}{2\pi kT}\right) \exp\left(-\frac{M}{2kT}\left(v_{xi}^2+(v_{zi}-v_{zo})^2\right)\right), \tag{16}$$

and $x_e$ is given by

$$x_e = x_o + \alpha v_{xi} + \beta v_{zi}. \tag{17}$$

The distribution of particles in the exit focal plane is given by

$$f = N\sqrt{\frac{M}{2\pi kT(\alpha^2+\beta^2)}} \exp\left[-\frac{M}{2kT}\frac{(x_e-\beta v_{zo})^2}{\alpha^2+\beta^2}\right] \tag{18}$$

which is also a Gaussian with a 1/e width given by

$$W = 2\sqrt{\frac{2kT(\alpha^2+\beta^2)}{M}}. \tag{19}$$

The conclusion to be reached with the aid of these simple examples is that the effects of the separate $v_x$ and $v_z$ dispersions, although additive for a single ion, are not additive for a distribution of ions. In fact, as in the previous example, the combined effect is such that the 1/e width is the root mean square of the individual 1/e widths. In practice, the dispersion will be a complicated function of $v_{xi}$, $v_{zi}$, $x_i$, M, and Q and may be discontinuous because of the slits. It is not practical to perform the integration analytically in order to determine the distributions in the exit focal plane. For this reason, a computer program has been employed.

3. Description of the Computer Program

The computer program consists of the solution to the equations of motion for ions in the instrument as a function of their mass, charge, initial position and velocity, with the dimensions and field strengths of the instrument left as parameters that may be changed from time to time. There are five important regions through which an ion can pass: Accelerator, Drift Sector 1, Electric Sector, Drift Sector 2, and Magnetic Sector. The dimensions and field strengths were obtained from the manufacturer, and the equations of motion were solved analytically for each of the 5 sectors; given the position, velocity, mass, and charge of an ion at the input of a given sector, the output position and velocity was determined. Those ions striking a slit were automatically rejected. The effects of fringing fields were also neglected.

VE=815

INITIAL DISTRIBUTIONS

X1= 0. , 0. .   VX1= 0. , 0. .   VZ1= 5.0,495.0J   N= 99.

NUMBER OF PARTICLES LOST= 0

FINAL X DISTRIBUTION

| | | | | | |
|---|---|---|---|---|---|
| .44324187E 00 | .44324187E 00 | .44324187E 00 | .44324187E 00 | .44324187E 00 | .44324187E 00 |
| .44324186E 00 | .44324187E 00 | .44324188E 00 | .44324187E 00 | .44324188E 00 | .44324188E 00 |
| .44324188E 00 | .44324189E 00 | .44324189E 00 | .44324191E 00 | .44324191E 00 | .44324191E 00 |
| .44324191E 00 | .44324192E 00 | .44324193E 00 | .44324193E 00 | .44324193E 00 | .44324195E 00 |
| .44324196E 00 | .44324196E 00 | .44324197E 00 | .44324197E 00 | .44324198E 00 | .44324199E 00 |
| .44324200E 00 | .44324201E 00 | .44324202E 00 | .44324202E 00 | .44324204E 00 | .44324206E 00 |
| .44324205E 00 | .44324208E 00 | .44324209E 00 | .44324210E 00 | .44324211E 00 | .44324213E 00 |
| .44324214E 00 | .44324215E 00 | .44324216E 00 | .44324218E 00 | .44324219E 00 | .44324220E 00 |
| .44324223E 00 | .44324223E 00 | .44324225E 00 | .44324226E 00 | .44324228E 00 | .44324229E 00 |
| .44324230E 00 | .44324233E 00 | .44324235E 00 | .44324237E 00 | .44324238E 00 | .44324240E 00 |
| .44324242E 00 | .44324244E 00 | .44324245E 00 | .44324247E 00 | .44324249E 00 | .44324251E 00 |
| .44324253E 00 | .44324256E 00 | .44324258E 00 | .44324259E 00 | .44324261E 00 | .44324264E 00 |
| .44324266E 00 | .44324268E 00 | .44324270E 00 | .44324272E 00 | .44324274E 00 | .44324278E 00 |
| .44324280E 00 | .44324281E 00 | .44324284E 00 | .44324286E 00 | .44324289E 00 | .44324291E 00 |
| .44324294E 00 | .44324297E 00 | .44324299E 00 | .44324302E 00 | .44324305E 00 | .44324308E 00 |
| .44324309E 00 | .44324312E 00 | .44324315E 00 | .44324318E 00 | .44324322E 00 | .44324324E 00 |
| .44324327E 00 | .44324330E 00 | .44324332E 00 | | | |

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EACH FREQUENCY BAR HAS BEEN SCALED BY   1.00000      EACH BAR IS  .97354253E-07      UNITS APART.
 .44324186E 00     XXXXXXXXXXXXXXXXXXXXXXXXXX
 .44324196E 00     XXXXXXXXXX
 .44324205E 00     XXXXXXXX
 .44324215E 00     XXXXXXX
 .44324225E 00     XXXXX
 .44324235E 00     XXXXXX
 .44324244E 00     XXXXX
 .44324254E 00     XXXXX
 .44324264E 00     XXXXX
 .44324274E 00     XXX
 .44324283E 00     XXXX
 .44324293E 00     XXXX
 .44324303E 00     XXXX
 .44324312E 00     XXX
 .44324322E 00     XXXX
 .44324332E 00     ----------------------------------------------------------------------------------------------------
                  0    5    1    1    2    2    3    3    4    4    5    5    6    6    7    7    8    8    9    9    1
                            0    5    0    5    0    5    0    5    0    5    0    5    0    5    0    5    0    5    0
                                                                                                                   0
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The final position of a given particle was obtained and tabulated, and a histogram subroutine was employed to plot the exit distribution of a given input distribution of ions. A random number generator was also available for choosing random initial distributions.

A sample of the computer output is shown above. The initial distribution chosen was 99 ions, having M = 131 AMU Q = $1.602 \times 10^{-19}$ coulombs, with $x_i = 0$, $v_{xi} = 0$, and $v_{zi} = 5, 10, 15 \ldots 495$ meters/second. The dimensions and typical field strengths of the CEC 21-110 were read in as parameters. The upper table shows the locations of the ions in the exit plane in meters with velocities increasing from left to right. The histogram above shows the distribution of ions in the exit plane; the "x"'s denote ions on the horizontal axis, and the vertical axis is the displacement in the exit plane in meters. Fifteen divisions were chosen for computing the histogram. The distribution corresponds to a quadratic or higher order dispersion in $v_{zi}$, since the slower ions are bunched around the smaller $x_e$ values.

4. Further Projects

With the aid of the computer simulation, more sophisticated experiments will be attempted. The first is the demonstration that the computer program is an accurate simulation of the actual mass spectrometer: this involves adjusting the parameters given to the computer so that the simulation will correspond as closely as possible to the actual instrument. Once the parameters have been set, it will be feasible to determine whether or not the resolution can be improved by changing the parameters. It will also be important to determine the smallest detectable mass difference on the basis of a reasonable assumption regarding the initial distribution of positions and velocities. Finally, the possibility of convolving the exit distribution from an arbitrary initial distribution with the theoretically expected distribution will be investigated as a means of improving the resolution.

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