A New Method for Plotting Exponentially Scanned Spectra on a Linear Mass Scale

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A new method for plotting linearized spectra from an exponentially scanned magnetic mass spectrometer on a strip chart recorder has been developed. The chart paper is advanced by a pulse motor which is fed from V/F converter, the input signal of which is proportional to the square of the scanning signal. The scanning speed can be varied without changing the linear mass scale on chart.

The linearity is sufficient to interpolate mass numbers over a span of one hundred mass units.

1. Introduction

Data acquisition methods using computers are today becoming more and more common in the field of mass spectrometry. Conversely, analog plotting of mass spectra with a potentiometric recorder has become almost obsolete. A simple mass spectrometer, however, equipped with a strip chart recorder is also an important tool for scientists, even though the recording speed is slow and the digitization of spectra from the recorded chart is very time consuming.

It is advisable to reduce this disadvantage by scanning the magnetic field exponentially. In this case the mass scale of the recorded spectra is usually not linear and it is not easy to assign its mass number on the chart.

In order to obtain a linear mass scale for exponential scanning, X-Y recorders were used^{1, 2, 3)}, the X-axes of which were driven by voltages proportional to the square of the mass number. The chart length of an X-Y recorder, however, is limited and it is not suitable for recording the spectra of the wide mass range.

Recently, a strip chart recorder with the chart paper advanced by a pulse motor has become commercially available. Its chart speed can be continuously varied by the electronic method. By using this type of recorder mass spectra can be plotted on a linear mass scale while the analyzing magnet is exponentially scanned.

2. Exponential Scanning

A linear mass presentation for a magnetic scanning instrument with a conventional X-t recorder is obtained when the magnetic field is scanned proportionally to the square root of the time. In this scanning mode the spectral line widths decrease with decreasing masses, since the resolving power is constant for all masses. Therefore, the recorder pen can not follow the input signal accurately in the low mass region.

When we give priority to the response time over the linearity of the mass scale, the best scanning mode is exponential scanning. Details are given as under.

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Let the image width at the collector slit be W_1 and the collector slit width W_2 , the time required for plotting one mass peak Δt is given by

$$\Delta t = t_p \frac{W_1 + W_2}{W_1} \quad (1)$$

where t_p is the time needed for reaching to the top of the peak from the bottom.

The resolving power R is defined as

$$R = \frac{m}{\Delta m} \quad (2)$$

where Δm is the mass difference between the start point and the end point of a mass peak at the mass number m .

Then the scanning speed dm/dt is written as

$$\frac{dm}{dt} \div \frac{\Delta m}{\Delta t} = \frac{mW_1}{t_p \cdot R(W_1 + W_2)} \quad (3)$$

or

$$\frac{dm}{m} \div \frac{W_1}{t_p \cdot R(W_1 + W_2)} dt.$$

If t_p is equal to the inherent rise time of the recorder and the analyzing magnet is scanned according to the relation (3), each mass peak will be plotted with its maximum speed.

Integration Eq. (3), we obtain

$$m = m_0 \exp \frac{W_1}{t_p \cdot R(W_1 + W_2)} t, \quad (4)$$

that is the exponential scanning.

This relation can be written as

$$m = m_0 \exp \frac{W_1}{t_p \cdot D_m} t,$$

where D_m is the dispersion coefficient.

3. Linear Mass Presentation

In order to facilitate the mass assignment on the chart, linear display is most desirable.

Mathematically this condition is written as

$$\frac{dy}{dt} = \frac{dm}{dt} \quad (5)$$

where dy/dt is the chart speed at any moment.

Since the magnetic field strength, B , is proportional to the square root of mass and B varies exponentially, the derivative of B^2 is also proportional to B^2 . Therefore,

$$\frac{dy}{dt} \propto B^2 \quad (6)$$

This result shows that if the magnetic field is varied exponentially and the chart speed can be varied proportionally to B^2 , the mass peaks will be displayed on a linear mass scale.

We may write $B \propto \exp \alpha t$, then

$$\frac{dy}{dt} = K \cdot e^{2\alpha t}$$

Integrating the equation, we obtain

$$y = \frac{K}{2\alpha} (e^{2\alpha t} - 1). \quad (7)$$

Substituting the boundary conditions: $m = m_0$ at $t=0$, and $m = m_1$ at $t = t_1$, we obtain the chart length y_1 at $t = t_1$,

$$y_1 = \frac{K}{2\alpha} \frac{m_1 - m_0}{m_0}$$

As the mass scale is linear, the chart length should be given by

$$y_1 = d(m_1 - m_0),$$

where d is the distance on the chart for the unit mass difference. Therefore,

$$d = \frac{K}{2\alpha m_0},$$

$$\alpha = \frac{\ln(m_1/m_0)}{2t_1} \quad (8)$$

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4. Electronic Circuit

The scanning circuit and the control circuit for the chart motor is shown schematically in Fig. 1.

The chart paper of the recorder* we used was advanced by a pulse motor. It advances the chart paper at 2.5/60 mm per pulse, and responds up to 250 pulses per second. The maximum chart speed is therefore 10.4 mm/sec.

The scanning circuit consists of a linear scan generator and an exponential function generator. The linear scan generator consists of a precise voltage reference with its divider and an integrator which generates a linear scanning signal and feeds into the exponential function generator, the output signal of which is applied to the magnet power supply as a control signal on the one side, and fed into a squarer on the other side.

The output signal from the squarer is applied to the input of V/F converter through a voltage divider and an amplifier, and V/F converter generates pulse signals, repetition rate of which is proportional to its input signal.

The pulse signals are divided by a frequency divider and fed into the pulse motor which advances the chart paper.

Since K in Eq. (7) is the chart speed at $t = 0$, K is written as follows:

$$K = \frac{S \cdot P \cdot A \cdot V_s(m_0)}{C \cdot n}, \quad (10)$$

where

S (mm/pulse) : pulse motor characteristic,

P (pulses/volt) : transfer characteristic of V/F converter,

A : amplifier gain,

$V_s(m_0)$: output voltage of squarer at $t = t_0$, $m = m_0$,

n : dividing ratio of squarer output voltage,

C : dividing ratio of frequency divider.

Substituting Eq. (10) into Eq. (8) and considering the specifications of the recorder and V/F converter* we used, we obtain,

$$d = \frac{125}{3} \frac{V_s(m_0)}{m_0 \ln m_1/m_0} \frac{A}{C} \frac{t_1}{n}, \quad (11)$$

where t_1 is the time required for scanning from m_0 to m_1 .

The mass scale can be changed by changing A , C and n . In our case, C is chosen so as to feed the input level of the V/F converter as high as possible and fixed.

Since t_1 is inversely proportional to the step input voltage of the integrator, the divider of the step voltage and the divider of the output voltage of the squarer is ganged so as to keep t_1/n constant. In this way, the scanning speed can be changed without changing the mass scale on

Fig. 1. Schematic diagram of the circuit used to drive the chart motor.

* Yokogawa Electric Works, Ltd., Technicorder F, Type 3052

** Dynamic Measurements 801A.

the chart.

The mass scale is independently changed by selecting the gain A of the amplifier.

5. Discussion

The necessary time for scanning over a mass range depends on the scan functions, the mass ranges, the resolving powers and the response time of the recording pen. It is easy to understand that they are proportional to the response time t_p and the resolving power R . They are given as $2t_p \cdot R(m_1 - m_0)/m_0$, $4t_p \cdot R(\sqrt{m_1} - \sqrt{m_0})/\sqrt{m_0}$, and $2t_p \cdot R \ln(m_1/m_0)$, for parabolic, linear and exponential scanning, respectively, in the mass range from m_0 to m_1 . The scanning times are calculated and tabulated in Table 1 for various mass ranges and scan functions.

In a typical scanning range, for example, from 10 to 100, the scanning time for exponential is half the time for the linear and a quarter of the time for the parabolic.

The deviation from the linear mass scale results from several sources. We assumed that the magnetic field was proportional to its exciting current and regarded the control signal for the magnet power supply as the signal proportional to the field strength itself. Strictly speaking they are not in proportion. Proportion deteriorates due to the hysteresis and the saturation of the

magnet iron. This problem may be improved by measuring directly the magnetic field with a Hall element and applying the resulting signal to the chart motor controller. The error of the squarer is another source of nonlinearity.

These errors occur in the case of an X-Y recorder, too. In addition to them, the non-linearity of the integrator, the error of the exponential function generator and the nonlinearity of V/F converter are sources of the nonlinearity in this case.

It must be noted that exponential scanning is not only the method to be desired from the view point of the response time of the recorder, but also it is the necessary condition for plotting spectra on a linear mass scale with an X-t recorder. Therefore, even when mass spectrometer is rapidly scanned in the mass range, where the precise recording of peaks is not needed, it should be scanned exponentially. If it is scanned exponentially the mass scale is not altered in that range and it is easy to find out the timing in order to slow down the scanning speed so as thereafter to plot mass spectra precisely. This procedure is very effective in reducing the necessary scanning time.

The actual mass scan is shown in Fig. 2 as an example. In this chart the following three mass ranges are rapidly scanned: from 1 to 2, (strictly speaking from the time 1 finished to the time of the commencement of 2), from 2 to 11 and from 18 to 24.

The mass scale measured and calculated from a chart are shown in Table 2.

Since mass numbers can be regarded as integers for low resolution mass spectrometry, the linearity is sufficient to interpolate mass numbers over a span of one hundred mass units or so. However, the assignment of mass numbers down to two or three decimal places by interpolation is not accurate enough unless referring two adjacent masses.

Table 1. Scanning times for various mass ranges and scan functions.

Mass Range	Scanning Time (sec.)		
	Exponential	Linear	Parabolic
1— 50	391	1214	4900
1—100	461	1800	9900
1—500	621	4272	49900
11— 50	151	226	355
11—100	221	403	809
11—500	382	1148	4445

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Fig. 2. An actual mass spectrum. Times shown are the actual scanning times. In this chart the following three mass ranges are rapidly scanned: from 1 to 2, from 2 to 11 and from 18 to 24. If these mass ranges are not rapidly scanned, the scanning times become very long, which are shown in parentheses.

Table 2. Measured mass scale. The unit mass distance is the averaged one in each mass range.

Mass Range (m/e)	Measured Distance (mm)	Unit Mass Distance (mm/mass)
12—18	27.4	4.57
18—28	45.8	4.58
28—38	45.9	4.59
38—50	55.5	4.63
50—58	37.0	4.63
61—71	46.5	4.65
71—81	46.3	4.63
81—91	46.5	4.65
94—104	46.8	4.68
104—114	47.0	4.70
114—124	47.5	4.75
125—135	47.0	4.70
135—149	47.5	4.75
149—167	47.8	4.78
167—183	48.4	4.84

This system is very convenient for recording mass spectra, but limited to slow scanning. The linearized display on an oscillographic recorder is very convenient for GC-MS applications, and in this field exponential scanning is necessary owing to the response time of the galvanometer. Therefore, the development of a high speed recorder with a variable speed chart motor is required.

References

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