An Accelerating Voltage Scanning Mass Spectrometer

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Accelerating voltage scanning mass spectrometer was designed and constructed in order to obtain high speed scanning. The retarding type ion source was used in order to increase the extraction efficiency of the ion source at low accelerating voltage.

The constructed mass spectrometer is a modified Mattauch-Herzog double focussing one and the mass range from 12 to 500 is obtained by adopting two different ion paths in the magnetic field.

The results of scan time (faster than $50\mu\text{sec}/\text{mass}$), sensitivity ($10\text{pg}/1\mu\text{l}$ for benzophenone) and resolution are sufficient for practical use.

1. Introduction

There are many cases in GC/MS analysis that require high speed scanning or high speed repeated scanning such as that for mass fragmentography (M.F.)¹⁾. High speed scanning is also necessary for integrating ion monitor scanning which is often used recently in order to increase S/N ratios of GC recordings.

As for the magnetic field scanning GC/MS, the scan rate is limited to within a few hundred a.m.u./sec even if a laminated iron core is used. Much higher scan speed is obtainable in the electric field scanning GC/MS. The quadrupole mass filter is an apparatus using electric field scanning and the capability of high speed scanning is one of the merits of QP-GC/MS.

In the case of a magnetic sector type mass spectrometer, the electric field scanning is achieved by changing the accelerating voltage of ions. There are two difficulties in this case. One is the rapid decrease of ion current from the ion source at low accelerating voltage. The other is the problem of mass range. Since the mass range is determined by the voltage range, the obtainable mass range is only 7 times for the change of accelerating voltage ranging from 0.5KV to 3.5KV. This is too narrow comparing with the necessary mass range in GC/MS, for instance the mass range of 12~500.

In order to overcome the problem of decreasing in ion sensitivity at low accelerating voltage a retarding type ion source²⁾ was used. In this ion source, a

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negative high voltage is applied to the main slit. Ions are first extracted by high voltage and then decelerated to lower voltage after passing through the main slit. Thus the decrease in ion intensity at low accelerating voltage is avoided.

To get a wider mass range, two different ion paths are introduced in the magnetic field, one with large orbital radius and the other with a smaller one. A mass range of 50 times is obtainable by this method.

This paper describes a mass spectrometer of magnetic sector type which can cover a mass region of 12~580 by electric field scanning.

2. Apparatus

2.1. Retarding type ion source

Prior to designing the apparatus, the ion extracting efficiency of the ion source was investigated for different accelerating voltages (V_{ac}) in order to determine the scanning range of the apparatus.

The schematic diagram of the ion source and the lens system are shown in Fig. 1. Differing from the conventional ion source, the main slit (S_1) is insulated and a negative voltage (V_s) is applied on it. Ions are decelerated by the electric field between S_1 and the retarding plate (S_2) at the ground potential. The voltage applied between the ion chamber (C_1) and S_1 was always kept at 3.0 KV by means of a floating power supply.

The variation of the total ion current with V_{ac} was measured by a total ion monitoring electrode (TIC) which was placed at the front side of S_2 . The result is given by curve A in Fig. 2. To compare with

the ion extracting efficiency of the normal type ion source, the variation of the ion current at $V_s = 0$ was also measured. The result is given by curve B.

These tendencies are always the same when measured by perfluorokerosene (PFK)

B : Base plate
P : Stainless steel cylindrical pipe

Fig. 1. Schematic diagram of the ion source

Fig. 2. Extracting efficiencies of the ion source A: V_s on, B: V_s off

gas or residual gas. As it can be seen from Fig.2 improvement of the ion extracting efficiency is significant for the case $V_{ac} \geq 0.5$ KV.

From these results we may determine the lowest V_{ac} for practical use to be 0.5KV.

Beam profiles of two cases (V_s off, V_s on) were measured at several V_{ac} by using TIC. The dependence of beam profiles on the slit width(1.5~10 mm) and the positions of S_r (within several mm) were not detected explicitly.

2.2. Ion optics

The schematic diagram of the mass spectrometer is shown in Fig. 3.

The double-focussing system in the reverse sense is adopted in order to correct the decrease of resolution due to the increasing deviation of energy at low accelerating voltage.

Two ion orbits were introduced in order to extend the mass range for the

limited V_{ac} range(3.5KV~0.5KV). Orbit I (radius: 120 mm) is for high mass region from 80 to about 500 a.m.u., and orbit II (radius: 45 mm) is for low mass region from 12 to 80 a.m.u. Then the mass range is 12 to about 500 a.m.u. under the constant magnetic field of 6500 Gauss.

A cylinder condenser is placed as shown in Fig. 3. By this device ions flowing through orbit I and orbit II can be detected by a single electron multiplier detector. The ion flowing through different orbits are selected by switching the voltage of deflecting system attached to the detector.

2.3. Power supply

The block diagram of the power supply is shown in Fig. 4. The accelerating voltage should be scanned from 3.5KV down to 0.5KV.

It is rather cumbersome to implement an all transistorized power supply of high voltage. The circuit diagram of the high

Fig. 3. Schematic diagram of the double focussing mass spectrometer(in mm units).

Fig. 4. Block diagram of the control system of the apparatus

voltage power supply is shown in Fig. 5. Two high voltage transistors (for instance, Toshiba 2SC2124) are Darlington-paired and five units of them are connected in series. V_{ac} is divided equally among them.

Fig. 5. High voltage power supply

The output V_{ac} is controlled by a control signal applied to the terminal I in Fig. 5. The necessary potential for the ion source electrodes and the deflecting system are given from the voltage divider as shown in Fig. 5. The negative power supply is shown in Fig. 6.

Stabilities measured are as follows with respect to two power supplies,

Line regulation:

less than 1.0×10^{-5} within $\pm 10\%$
alternation of the input voltage.

Temperature coefficient:

less than $0.5 \times 10^{-4}/\text{deg}$

Ripple:

less than 1.0×10^{-3}

The mass spectrum is well known not to be linear when Miller integrator is used as a reference voltage. In order to obtain mass linear spectrum, a divider circuit ($1/V_{in}$) (for instance, Toshiba AD

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533) should be put after Miller integrator.

The switching of the high and low mass orbits is controlled alternately by the scanning control unit.

3. Results

3.1. Mass spectra

Mass spectra of PFK with respect to accelerating voltage scanning are shown in Fig. 7-a and 7-b. The spectrum in Fig. 7-b is that of orbit I (high mass region) and the spectrum in Fig. 7-a is that of orbit II (lower mass region).

The magnetic field strength is kept at 6600 Gauss and the accelerating voltages corresponding to mass numbers are shown in parentheses.

In order to examine the range of sensitivity for different accelerating voltages the same mass spectrum was taken by the magnetic field scanning mode where V_{ic}

Fig. 6. Negative voltage power supply

was kept at 3 KV.

From the comparison of the corresponding peak heights, the extracting efficiency at electric field scanning was estimated and the result is shown in Fig. 8.

3.2. High speed scanning

One of the merits of the electric field

Fig. 7. Mass spectra of perfluorokerosene

Fig. 8. Mass sensitivity
A: V_s on, B: V_s off

scanning is the capability of high speed scanning.

An oscilloscope was used in order to observe the mass spectrum. The input signal of the oscilloscope was taken directly from the output terminal of the electron

multiplier.

Results are shown in Fig. 9.

These spectra were taken together with the sawtooth wave form Miller integrator circuit. In Fig. 9 the scanning speed at mass number 400 a. m. u. was about $50\mu\text{sec}/\text{mass}$.

We can conclude from those observations that no distortion of mass peaks were observed, and that practical high speed scanning time of 1000 a.m.u./0.5 sec could be realized.

3.3. Sensitivity

Absolute measurements of the apparatus' sensitivity were made by using gas chromatography (G.C.). G.C. was combined with the ion source by a Ryhage separator.¹⁾ The measurements were made by means of M-F by which a single peak was observed.

The measured calibration curves for benzophenone and methylstearate are shown

Fig. 9. Oscillograph images of perfluorokerosene at scanning of the accelerating voltage

in Fig. 10-a and 10-b, respectively.

The obtained sensitivities were 10pg/ $\mu\ell$ in Fig. 10-a and 20 pg/ $\mu\ell$ in Fig. 10-b, and the S/N ratios for both were about 3.5.

The linearity of calibration curves was satisfactory. The results for both sensitivity and linearity are sufficient for practical use.

3.4. Resolution

The resolution was measured for tow cases.

One was the case of the straight magnetic field boundary and the other of the curved boundary at the exit side.

The resolution (Rth) is given theoretically by the equation.

$$R_{th} = am \cdot Am / (X \cdot Wi + Wc + \mathcal{A})$$

Am: Mass dispersion(0.5)

X: Image multiplication in the horizontal plane(0.5)

Wi: Ion source slit width

Wc: Collector slit width

$\mathcal{A}$: Total aberration

The total aberration($\mathcal{A}$) is given by the equation.

$$\mathcal{A} = am \cdot (|A_{\alpha\alpha}\alpha_0^2| + |A_{\alpha\delta}\alpha_0\delta_0| + |A_{\delta\delta}\delta_0^2| + |A_{yy}(y_0/am)^2| + |A_{y\beta}(y_0/am)\beta_0| + |A_{\beta\beta}\beta_0^2|)$$

Where $A_{\alpha\alpha}$, $A_{\alpha\delta}$, $A_{\delta\delta}$, A_{yy} , $A_{y\beta}$ and $A_{\beta\beta}$ are the second order coefficients. The meaning of symbols α , δ , y , and β are as follows:

α : Divergent angle of ion beams in the horizontal direction.

δ : Energy spread of ion beams.

y : Ion source slit width in the ver-

Fig. 10. Calibration curves

tical direction.

β : Divergent angle of ion beam in the vertical direction.

The second order aberration coefficients are calculated by TRIO³⁾ (Table I).

In case of V_s off α_0 , δ_0 , y_0 and β_0 are estimated as follows.

$$\alpha_0 = 6.5 \times 10^{-3} \text{ rad}$$

$$\delta_0 = 3.3 \times 10^{-4}$$

$$y_0 = 1.5 \text{ mm}$$

$$\beta_0 = 2.0 \times 10^{-3} \text{ rad}$$

In case of V_s on, only δ_0 is changed in the following ways.

$$\delta_0 = 3.3 \times 10^{-4} \times 3000 / \text{Vac} = 0.99 / \text{Vac}$$

Table I. Aberration coefficients calculated by TRIO.

	Case A	Case B
$A_{\alpha\alpha}$	0.556	0.190
$A_{\alpha\delta}$	3.75	3.90
$A_{\delta\delta}$	-0.172	-0.188
A_{yy}	-0.531	-0.345
$A_{y\beta}$	-4.46	-2.91
$A_{\beta\beta}$	-9.32	-6.10

Case A: Straight boundary

Case B: Curved boundary at the exit side
radius of concave curvature: 240 mm

Table II. Values of Rth and Rex.

	Scan mode	$d(\mu\text{m})$	Rth	Rex	Wi(mm)
A	Mg Scan*	33	450	450	0.1
	Vac Scan*	33	720	740	0.05
	Vac Scan**	40	660	660	0.05
B	Vac Scan*	21	840	770	0.05
	Vac Scan**	28	770	670	0.05

Examined mass number are 367 and 369 for magnetic field scan (Mg scan), and 502 and 503 for accelerating voltage scanning (Vac scan).

Vac at Mg scan is 3.0 kV and Vac at Vac scan is 0.6 kV.

Case A: Straight boundary

Case B: Curved boundary at the exit side

* : V_s off, ** : V_s on

δ_0 can be estimated at 1.7×10^{-3} with respect to the mass number 502 and 503 (Vac, 0.6 kV) at which measurements were made. The obtained resolutions (Rex) are shown in Table II with the estimated values of d .

We are able to conclude from the results that the agreement of Rth and Rex is satisfactory. The typical peak shapes are shown in Fig. 11.

Fig. 11. Peak shapes(M/Z: 502, 503)

Sample: Perfluorokerosene+perfluoro-tributylamine

a, b : Straight boundary

c, d : Curved boundary at the exit side

a, c : V_s off, b, d : V_s on

3.5. Mass marker

It is very important to designate a mass number to every peak. As for the

magnetic field scanning type, this is done by means of Hall effect measurement and the calibration is rather difficult.

In the present apparatus, this can be done by measuring V_{ac} directly. The relationship between mass number (M) and V_{ac} is given by the following equation:

$$H_0 \cdot am = 143.9 \sqrt{M \cdot V_{ac}}$$

H_0 : Magnetic field strength in Gauss

am : Ion orbital radius in the magnetic field in centimeters.

M : Mass number in a.m.u.

V_{ac} : Accelerating voltage in volts.

When H_0 and am are fixed the signal for mass marking can be obtained from a simple electric circuit. Therefore this is quite advantageous comparing to the complexities of mass marking circuit with a Hall device.

Taking the mass peak at $M = 119$ as standard, the observed mass numbers are calculated from the above equation for each observed voltage (V_{ac}).

The results are shown in Table III. The agreement between the mass numbers

Table III. Observed mass numbers(M_{ob}) obtained from V_{ac} .

M	V_{ac} volt	M_{ob}	$M - M_{ob}$
119	93.851	Standard	
131	85.254	131.00	0.0
181	61.705	181.00	0.0
231	48.359	230.95	0.05
281	39.753	280.94	0.06
331	37.751	220.90	0.10
381	29.321	380.90	0.10
431	25.916	430.94	0.06
481	23.222	480.94	0.06
502	22.245	502.06	0.06

V_{ac} was obtained through the resistor deviding accelerating voltage (V_{ac}).

calculated from V_{ac} and the real mass numbers are very satisfactory. The accuracy of the mass marker (0.15 a.m.u) is better than that of the case using a Hall device which is about 0.3 a.m.u..

The reproducibility of mass marking during long period was also satisfactory (within 0.2 a.m.u.).

4. Conclusion

The advantages of the electric field scanning mass spectrometer using the present system are summarized as follows.

1. The change of the ion intensities for different accelerating voltages was not serious when using the retarding type ion source.
 2. The wide mass range of $12 \sim 580$ was obtained by using two different ion paths.
 3. The scanning speed as fast as $50 \mu\text{sec}/1$ mass was attained at the mass number of 400.
 4. The mass marking electronics was very simple and steady.
- The accuracy and the reproducibility was satisfactory.
5. Since the scan speed is very fast, the survey of metastable ions in collision induced dissociation may be possible by repeated scanning of V_{ac} for various electric field potentials.⁴⁾

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References

- 1) W. Mcfaden, "Techniques of Combined Gas Chromatography/Mass Spectrometry, Applica-

- tion in Organic Analysis", 1973. John Willey and Sons, New York (1973), p. 252.
- 2) I. Katakuse, T. Matsuo, H. Nakabushi and H. Matsuda, *Mass Spectrosc. (Japan)*, **25**, 211 (1977).
- 3) T. Matsuo, H. Matsuda, Y. Fujita and H. Wollnik, *ibid.*, **24**, 19 (1976).
- 4) R. K. Boyd and J. H. Beynon, *Org Mass Spectrom.*, **12**, 163 (1977).

Keywords

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