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ORIGINAL PAPERS**Determinations of Gains of Electron Multiplier
by Pulse Counting Method**

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A pulse counting method has been used to determine gains of an electron multiplier for various ions. A 16-stage box and grid type electron multiplier with copper-beryllium dynodes has been employed in equipment to a single focusing mass spectrometer. The condition, where the gain determined by the pulse counting method becomes almost identical to that by a Faraday cup method for each of various ions, has been discussed.

1. Introduction

Gains of an electron multiplier for interesting ions are important factors in determinations of vapor pressures of materials by a mass spectrometric Knudsen effusion method. Usually, gains are experimentally determined by the Faraday cup method. However, applications of this method are only allowable to rather intense ions.

For weak ions whose intensities are too low to determine gains by the Faraday cup method, values of gains have been estimated by the inverse square root approximation¹⁾ and also by the interpolation of a calibration curve which is obtained by relating gains for several intense ions to square roots of their atomic mass units²⁾.

In some cases, gains for weak ions have been assumed to be identical to that for the intense ion of a similar chemical form to interesting ions³⁾.

To determine gains for weak ions experimentally, Kohl and Stearns⁴⁾ have used a pulse counting method. The output from the anode of the multiplier is brought to a picoammeter or alternatively to an ion pulse counting system. The current I_a measured by the picoammeter is related to the number of ions incident on the first dynode of the multiplier as follows,

$$G_e = \frac{I_a}{Ne}, \quad (1)$$

where G_e is the gain determined by the pulse counting method, N is the number of ions per second striking the first dynode, that is, the ion counting rate measured by

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the pulse counting system and e is the charge of the electron. Thus, the gain may be determined by using Eq. (1).

The present paper is described many informations on comparisons of gains determined by the pulse counting method with those by the Faraday cup method. Kohl and Stearns⁴⁾ have reported that in their experimental condition the gain for gold ion by the pulse counting method is about 13 per cent as low as one by the Faraday cup method. As will be shown later, however, in the present condition the agreement between the gain determined by the pulse counting method and one by the Faraday cup method is excellent for each of various ions.

2. Experimental

Figure 1 shows a block diagram for the pulse counting system and the direct current measuring system used in the present investigation. A 16-stage box and grid type electron multiplier with copper-beryllium dynodes (Hamamatsu R 596) was employed in equipment to a single focusing

Hitachi RM-6K mass spectrometer.

The output from the anode of the multiplier was brought to either a Keithley 417 picoammeter in the case of direct current measurements or an ORTEC 124 low-noise charge-sensitive preamplifier in pulse counting measurements. In latter measurements, an ORTEC 450 research amplifier was followed as a linear amplifier. Since the pulse height distribution for an ion was enough wide, both of the counting efficiency and pulse height distribution were almost independent of the choice of the integrate time constant for pulse shaping. The differentiate time constant was positioned to $2\mu\text{sec}$ in order to avoid any pile-up effect. The counting of pulses and their pulse height distributions were measured by the use of a Canberra 8100 multichannel analyzer.

The counting rate was monitored with an ORTEC 449 log/lin ratemeter. The energy linearity and the resolution of the pulse counting system were checked by the use of an ORTEC 419 precision pulse generator.

Fig. 1. Diagram for pulse counting system and direct current measuring system.

3. Results and Discussion

In order to improve signal to noise ratio of the pulse counting system, the background counting rate is usually diminished as low as possible by setting the discriminator level to greater position than zero division. However, the apparent counting efficiency for an ion decreases with increasing the position of the level. Furthermore, as have been pointed out by Miyake⁵⁾ and Ono, *et al.*,⁶⁾ pulse height distributions for various ions are also different with their atomic mass units. In the present system, the distribution for a residual gas ion of $m/e=57$ was the widest and distributions for heavier ions and for lighter ions than the $m/e=57$ became narrower. From these reasons, the discriminator level was positioned to zero division. In this position, background counting rates were 0.2, 0.1, 0.05 and 0.003 cps at applied voltage to the multiplier being 2.4, 2.2, 2.0 and 1.8 kV, respectively.

The value of G_c for an ion at a given applied voltage to the multiplier was obtained from Eq. (1) by measuring the pulse counting rate and the direct current of the ion under the condition where the ion intensity was controlled to be 100cps order of magnitude or 10^{-17} A with the current of the ionizing electron. Consequently, the determination of G_c might be made without the decrease of the apparent counting efficiency and serious effects of pile-up and of background counting rate.

The background counting rate is strongly depended upon the residual gas pressure in the range above 3×10^{-4} Pa,⁷⁾ but the dependence becomes much less bellow 2×10^{-5} Pa,⁸⁾ where the present investigation

has been made.

The determination of the gain G_F by the Faraday cup method was made as follows. At a given applied voltage to the multiplier, the direct current I_a from the anode of the multiplier was measured, and after the applied voltage was turned off, the current $I_{1 \text{ and } 2}$ from both first and second dynodes of the multiplier was measured. In the latter measurement, the emission of secondary electrons from the first dynode was suppressed by applying -22.5 V to a grid in front of the first dynode. The value of G_F may be thus determined by the following equation,

$$G_F = \frac{I_a}{I_{1 \text{ and } 2}}, \quad (2)$$

It has been pointed out by Grimley⁹⁾ and Inghram, *et al.*,¹⁰⁾ that the number of electrons produced by the impingement of an ion on the first dynode are varied with the ion accelerating voltage, the mass of the ion, the ionic charge, the electronic configuration of the ion, the chemical composition of the ion and the angle with which the incident ion strikes on the first dynode. Furthermore, the multiplication of these electrons for each of the stages is almost linearly increased as the applied voltage to the multiplier increases.¹¹⁾ Among these factors, the dependence of the ion accelerating voltage on values of G_c and G_F for $^{18}\text{H}_2\text{O}^+$ ion was investigated. The results at an applied voltage of 2.0kV to the multiplier are shown in Fig. 2. As will be predicted from the literature,¹⁰⁾ values of G_c and G_F become larger with increasing the ion accelerating voltage. While ratios of G_c to G_F decrease very

Fig. 2. Dependence of ion accelerating voltage on gain of electron multiplier for $^{18}\text{H}_2\text{O}^+$ ion. Applied voltage to electron multiplier: 2.0 kV.

slightly; those are varied from 1.06 at an ion accelerating voltage of 1.2 kV to 1.00 at 4.8 kV.

In Fig. 3 is shown the dependence of the applied voltage to the multiplier on values of G_c , G_F and G_c/G_F for $^{18}\text{H}_2\text{O}^+$ ion at an ion accelerating voltage of 4.8 kV. Values of logarithms of G_c and G_F are almost linearly increased with increasing the value of the logarithm of the applied voltage to the multiplier. The number of effective stages of the multiplier is determined from slopes of lines in Fig. 3 to be 7.6 by the pulse counting method and to be 7.9 by the Faraday cup method, but these are considerably smaller than the number of actual stages. Aratani and Saito¹¹⁾ have reported that the number of effective stages of their 10-stage copper-beryllium electron multiplier is determined

by the Faraday cup method to be 6. This value is also smaller than the actual number like as present results.

Fig. 3. Dependence of applied voltage to electron multiplier on its gain for $^{18}\text{H}_2\text{O}^+$ ion. Ion accelerating voltage: 4.8 kV.

The dependence of the applied voltage to the multiplier on the ratio of G_c and G_F is severe as seen in Fig. 3, where ratios are much larger than unity at applied voltages below 2.0 kV and conversely ratios are smaller than unity above 2.0 kV. However, the ratio becomes equal to unity at an applied voltage of 2.0 kV. Namely, these results show that when the ion accelerating voltage is held at 4.8 kV and the applied voltage to the multiplier is held at 2.0 kV, the pulse counting method may be used to determine the gain being identical to one by the Faraday cup method.

Under the condition mentioned above,

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Table 1. Gains of electron multiplier for various ion species.

Ion accelerating voltage: 4.8 kV.

Applied voltage to electron multiplier: 2.0 kV.

Ion Species	$G_c(\times 10^6)$	$G_F(\times 10^6)$	G_c/G_F
$^1\text{H}^+$	0.82	0.80	1.03
$^2\text{H}_2^+$	1.09	1.19	0.92
$^7\text{Li}^+$	0.79	0.78	1.01
$^{18}\text{H}_2\text{O}^+$	1.07	1.07	1.00
$^{28}\text{N}_2^+$	1.13	1.17	0.97
$^{28}\text{CO}^+$	1.18	1.14	1.04
$^{30}\text{Li}_2\text{O}^+$	1.25	1.22	1.02
$^{32}\text{O}_2^+$	1.17	1.16	1.01
$^{40}\text{Ca}^+$	0.77	0.78	0.99
$^{44}\text{CO}_2^+$	1.15	1.11	1.04
$m/e=57$	1.18	1.18	1.00
$m/e=71$	1.16	1.15	1.01
$m/e=85$	1.04	1.03	1.01
$^{107}\text{Ag}^+$	0.58	0.56	1.04
$m/e=129$	1.01	1.02	0.99
$^{138}\text{Ba}^+$	0.55	0.52	1.06

values of G_c , G_F and G_c/G_F for various ions originated from residual gases in the ion source and from vapors effusing from Knudsen cells were determined. Table 1 shows results obtained for 16 kinds of ion species. These are all taken for singly

charged ions. As can be seen in Table 1, values of gains are varied with kinds of ion species, while ratios of G_c to G_F for various ions are almost equal to unity; in other words, the agreement between values of G_c and G_F is in excellent for each of various ions.

In Fig 4. is shown the relation of gains for various ions given in Table 1 to square roots of their atomic mass units. The important observations seen in Fig 4. are that i) gains decrease as the atomic mass units increase, ii) gain for a molecular ion is larger than that for an atomic ion at the same supposed mass unit and iii) the drawing of an accurate calibration curve is difficult by the use of gains for ions of different chemical compositions. Thus, gains for weak ions whose intensities are too low to determine gains by the Faraday cup method should be experimentally determined by the pulse counting method such as described in the present investigation.

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Fig. 4. Relation of gains of electron multiplier for various ion species to square roots of their atomic mass units. Ion accelerating voltage: 4.8 kV. Applied voltage to electron multiplier: 2.0 kV.

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Keywords

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