The Secondary-emission Electron Multiplier Tube Used on a Mass Spectrometer and its Amplification of Ion Currents

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The requirement for a detector both reliable and very sensitive for the measurement of ion beam currents in mass spectrometry has greatly increased in the past few years. This requirement can be attributed largely to the following:

1. Studies of the measurement of ionization potentials, especially by means of the ionization produced by vacuum-ultraviolet light.
2. The measurement of very small amounts of inert gases occluded in minerals or meteorites in order to determine their age.
3. The mass spectrometric measurement of ions produced by the alpha-ray in the study of ion-molecular reactions.

Various types of electrometers and electrometer tube amplifiers have been used to measure the ion currents collected by the Faraday cage of the mass spectrometer. By such means, ion currents as low as 10^{-14} amp. have been detected. Probably the best commercially available device for the reliable measurement of very small ion currents is the vibrating-reed electrometer, but this instrument has two important limitations which cause trouble at low input currents. First, the time constant of the input reed circuit increases to about 1 sec. when a 10^{11} ohms resistor is used, and, second, the alpha particle activity of about 1 alpha particle per 2 min., which results from the radioactive elements present in the vibrating-reed head in trace amounts, gives rise to bursts of charge. It is generally accepted that the measurement of very small ion currents of less than 10^{-16} amp. are extremely difficult to measure by ordinary methods.

In order to carry out this type of measurement, the secondary-electron emission multiplier is useful. Several types of electron multipliers have been used in mass spectrometry, namely, the electro-static focused multiplier[1-3], the magnetic focused multiplier[4,5], and the scintillator type multiplier[6,7]. The construction of the electrode system in the magnetic-focused electron multiplier is simple, but the preparation of the emitter of the secondary electrons is difficult. On the scintillator type multiplier, a scintillator fit to use in high vacuum conditions is difficult to obain. The electro-static focused type electron multiplier is considered to be the most convenient for use as an amplifier of very small amounts of ions in mass spectrometric studies. The author has already investigated the characteristics of the secondary electron emission by positive ions from the surface of copper-beryllium for the purpose of making use of the dynode

1) R. E. Halsted and A. O. Nier, *Rev, Sci. Instr.*, **21**, 1019 (1950); M. J. Higatsberger, H. L. Demorest and A. O. Nier, *J. Appl. Phys.*, **25**, 883 (1954).
2) J. S. Allen, *Phys. Rev.*, **55**, 966 (1939); *Rev. Sci. Instr.*, **18**, 739 (1947).
3) F. A. White and T. L. Collins, *Appl. Spectroscopy*, **8**, 17, 169 (1954).
4) L. G. Smith, *Rev. Sci. Instr.*, **22**, 3, 166 (1951).
5) L. Heroux and H. E. Hintereger, ibid., **31**, 280 (1960).
6) P. I. Richards and E. E. Hays, ibid., **21**, 99 (1950).
7) N. R. Day, ibid., **31**, 264 (1960).

material for the electro-static focused type secondary electron multiplier[8-10].

There are, in the literature, a large number of papers reporting investigations of the characteristics of the electron multiplier, but many of these papers are contradictory because of the large number of variables involved in this phenomenon[11]. Thus, with respect to the reported results concerning the mass dependency of the amplification factor of the electron multiplier for various ions, Nier et al.[1] have reported that its multiplicity for inert gas ions is inversely proportional to the square root of the ion mass, while, on the other hand, White and Collins[3] have reported that the multiplicity of the electron multiplier is independent of ion mass, and Barnett et al.[12] have produced evidence which purports to show that the mass dependency of the multiplicity of the electron multiplier depends on the conditions for treating the dynodes.

In this study, the author has designed and constructed a 12-stage secondary electron multiplier tube using copper-beryllium dynodes treated with electro-polish and with activation by oxidation, and the electron multiplier so constructed has been installed to with the mass spectrometer. The amplification factor of the secondary electron multiplier for inert gas ions has been measured as a function of the supplied voltage to the conversion dynode of the electron multiplier, and the results have been compared with those obtained with the multiplier using electro-polished and activated dynodes. The best amplification was obtained 2×10^5 by the electron multiplier constructed with activated dynodes for helium ions.

Experimental

The Mass Spectrometer its Reconstruction.—In this study, the instrument used was a modified Hitachi RMC-1 type mass spectrometer, which is of the 90° sector type, its radius of the curvature of the ion path and its maximum resolution in mass units being 135 mm. and 150 respectively.

In order to install the secondary electron multiplier and to determine the amplification factor of the ion current by the secondary electron multiplier, the collector block of the mass spectrometer was reconstructed of stainless steel, as is shown in Fig. 1. As may be seen in Fig. 1, the 96 mm. square collector block was welded to the analyzer tube in order to have the center of the collector block deviate by 10 mm. from the center of the analyzer tube. In Fig. 1, S_E and S_S are the earth slit and the suppresser plate for the Faraday cage F respectively. The width of the earth slit is variable over a range from 0 to 5 mm. by means of the driving screw, shown as D.S. in the diagram. The Faraday cage, F, may be moved a distance of 30 mm. without breaking the vacuum condition, for the purpose of measuring the amplification factor of the electron multiplier in the same ion path. After removing the Faraday cage, the electron multiplier tube can approach the earth slit, S_E, shown in Fig. 1. The maximum range of displacement of the electron multiplier tube is 30 mm. The electron multiplier was assembled on the E. M. flange by the method described below.

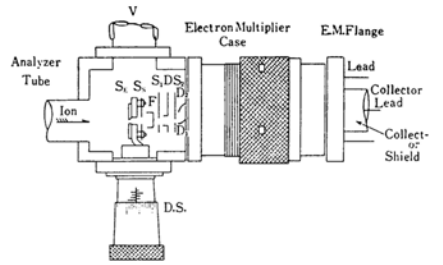

Fig. 1. Schematic diagrams of the collector block of the mass spectrometer and the electron multiplier. D.S. is the driving screw for variation of the width of the earth slit S_E, V is the pumping line, S_S is suppressor plates for secondary electrons from Faraday cage F, S_1, D, S_2, D_1 and D_2 are entrance slit of the ion beam, ion deflecting plate, second entrance slit, conversion dynode and second dynode of the electron multiplier, respectively.

Electron Multiplier Tube Design.—The electron multiplier tube was designed by reference to the electron multiplier used by Nier et al.[1] * The assembly and the details of the actual electrode system of the electron multiplier are shown in Fig. 2. In Fig. 2, B, S_E, S_S and F are the baffle slit, the earth slit, the suppressor plate for secondary electrons from the Faraday cage and the Faraday cage respectively. To the right of S_1 in Fig. 2, the assembly of the electrodes of the electron multiplier is shown. In Fig. 2, S_1 and S_2 are disks, 40 mm. in diameter and 1 mm. in thickness, made from stainless steel; each disk has an entrance slit of 10×3 mm^2 for the ions; D indicates the ion deflector plates, that were constructed from two plates, 4×10 mm^2 in area, installed parallel to each other at a distance of 7 mm. D_1 is the conversion dynode which gives off secondary electrons which are accelerated and focused onto a second dynode, D_2. The electrodes from D_2 to D_{12} are a succession of dynodes which give off multiplied secondary electrons which are accelerated and focused onto the following dynode. These dynodes are pressed from a copper-beryllium plate, 0.2 mm. in thickness,

8) T. Sugiura and T. Hayakawa, This Bulletin, **34**, 58 (1961).
9) T. Sugiura, ibid., **34**, 1475 (1961).
10) T. Sugiura, ibid., **35**, 218 (1962).
11) M. G. Inghram, "A Handbook on Mass Spectroscopy", National Academy of Sciences (1954), p. 41.
12) C. F. Barnett, G. C. Evods and P. M. Stier, *Rev. Sci. Instr.*, **25**, 1112 (1954).

* The details of the specifications of the multiplier tube are from a private communication from Professor A. O. Nier to Professor K. Ogata of Osaka University.

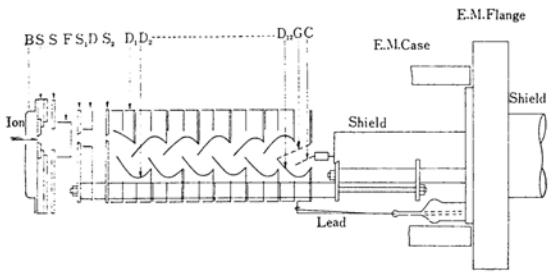

Fig. 2. Schematic diagram of the secondary-emission electron multiplier tube. B, S_E, S_S and F are the buffle slit, earth slit, suppressor slit and movable Faraday cage, respectively. S_1, D, S_2 are the entrance slit for the ion beam, ion deflecting plates, and second entrance slit of the electron multiplier tube, respectively. D_1 is the conversion dynode, the electrodes indicated from D_2 to D_{12} are succeeding dynodes, C and G are the electron collector and its shielding grid.

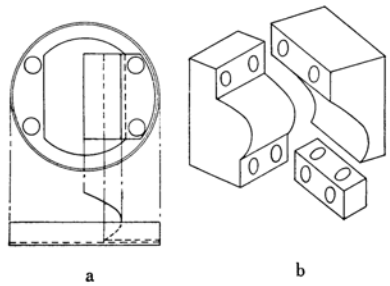

Fig. 3. Schematic diagram of a dynode of the electron multiplier and its shielding plate (a), and schematic view of the mold for shaping the dynodes of the electron multiplier (b).

in the mold shown in Fig. 3b. C and G in Fig. 2 are the electron collector and the shielding grid of the electron collector respectively. Both C and G are in the form of a grid made from tungsten wire 0.07 mm. in diameter, and the rim is made from stainless steel 0.1 mm. in thickness. The electron collector, C, is supported by a molybdenum rod fixed in the center of the E. M. flange by means of a glass-kovar seal. Each dynode was treated after shaping by the method described below, after which each dynode was put into the shielding plate, with a shielding rim 5 mm. in height and 0.3 mm. in thickness, as is shown in Fig. 3a; the shielding plates and the dynodes successively installed pass through four supporting rods, one on top of another, electrically insulated from each other by the quartz spacers. The supporting rods were made from stainless steel 3 mm. in diameter and covered by slender quartz tubes 4.8 mm. in outer diameter and 3.2 mm. in inner diameter. The quartz spacers, 6 mm. in length, were carved from a quartz tube 8 mm. in outer diameter and 5 mm. in inner diameter, and these quartz spacers were burnished up 1/100 mm. precision in length. The electrical connection for each dynode and electrode was provided from the fifteen lead connections

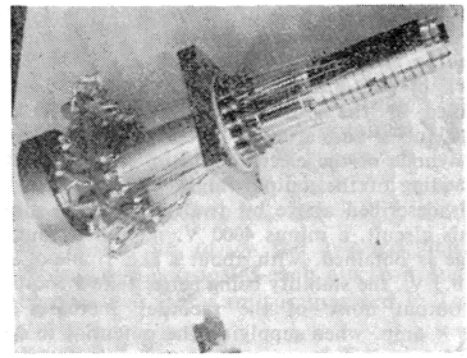

Fig. 4. The electrode structure of a electron multiplier tube used on a mass spectrometer, and the quartz insulators and dynode (lower part of the figure).

sealed by the glass-kovar seal surrounding the collector lead on the E.M. flange. In Fig. 4, a picture of the electron multiplier tube is shown, together with the quartz insulators and the dynodes.

Electronic Circuit for Supplying the High Voltage.—The electronic circuit for supplying a high voltage to each dynode of the secondary electron multiplier, as shown in Fig. 5, was constructed by the author himself. To obtain a high voltage, a commercially offered flyback-transformer was employed, as were a 6CM5 tube as a high frequency input supply for the flyback-transformer, and a 12AU7 tube as a symmetrical multi-vibrator for the rectangular input of the 6CM5 oscillator. The high voltage obtained by the flyback-transformer was rectified by a 1B3-GT tube and a simple RC filter. The oscillator, flyback-transformer, rectifier and RC filter were constructed

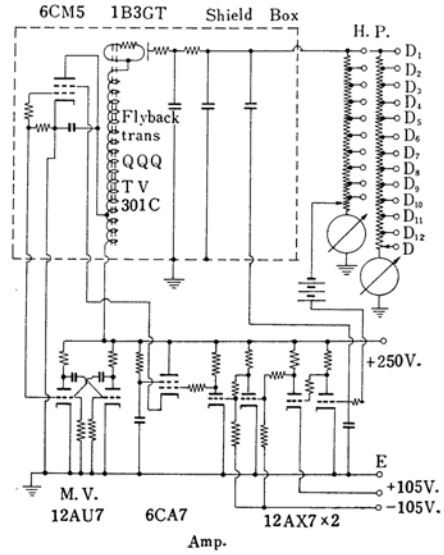

Fig. 5. Electrical circuit of the high potential supply for the electron multiplier tube. H.P. is the output of the high potential, M. V. is the symmetrical multivibrator using 12AU7 tube, Amp. is the d. c. amplifier.

in the shieled box, which was made from copper net. The output voltage was stabilized by means of feeding back to the screen grid of the oscillator a part of the output current after it had been amplified by the amplifier, which employed two 12AX7 tubes and a 6CA7 tube. The voltage to each dynode of the electron multiplier was supplied by dividing of the output high voltage from the circuit described above by twelve 3 MΩ resistors. By this circuit, a minus 4000 V. maximum output voltage is obtained, with about a 8kc. ripple of less than 0.1 V., the stability being better than 2.5×10^{-5}. The output noise of the recorder increases by 2×10^{-14} amp. when supplying the potential to each dynode.

Activation of Dynodes.—The apparatus for the activation of the dynodes of the electron multiplier has been described in previous papers[8,9]. The dynodes of the electron multiplier were activated in the following manner: The shaped and electro-polished dynodes were placed in a quartz tube and evacuated to higher than 5×10^{-6} mmHg at about 800°C for about three hours. Then the temperature of the quartz tube was lowered to 420°C, and oxygen was introduced at an initial pressure of 1 mmHg. After 20 min. the oxygen was pumped out, and the temperature was lowered to room temperature.

Experimental Procedure.—For the measurement of the ion and the amplified electron currents, a conventional type D.C. amplifier was used; this amplifier employed a HT-1005 tube, a modified 6C6 tube as a priamplifier tube, and a 6SN7 tube as a second-stage differential amplifier. For the recorder a four-element oscillo-galvanometer was used. In order to determine the total gain of the secondary electron multiplier, high resistances of 1×10^{10} ohms for direct measurement of the ion current and 1×10^{8} ohms for measurement of the electron current amplified by the electron multiplier were used in the circuit of the D.C. amplifier.

Results

The amplification factors of the 12-stage secondary electron multipliers, which are constructed from electro-polished copper-beryllium dynodes and from activated copper-beryllium dynodes, were obtained for inert gas ions, using different voltage supplies to the conversion dynodes. In Figs. 6 and 7, the amplification factors for the electron multiplier using inert gas ions are plotted as functions of the supplied voltage to the conversion dynode in the range from −1800 to −3000 V. In these

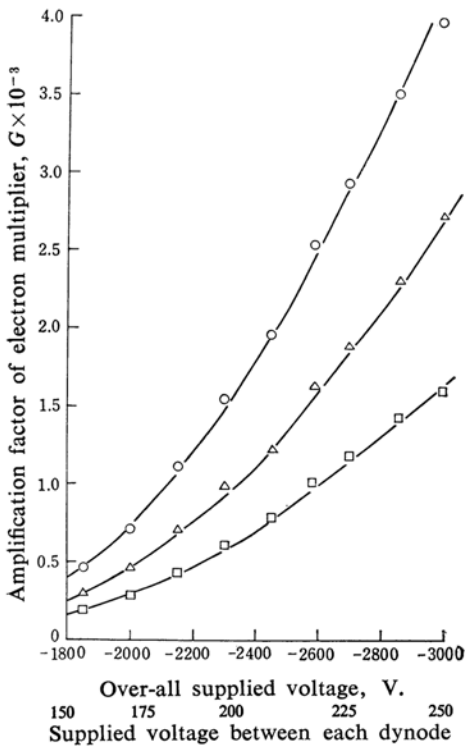

Fig. 6. Amplification factor of the electron multiplier tube using the electro-polished dynodes, as functions of supplied voltage to conversion dynode for inert gas ions. Circular, triangular and square points indicate results for $^{4}He^{+}$, $^{20}Ne^{+}$ and $^{40}A^{+}$ ions, respectively.

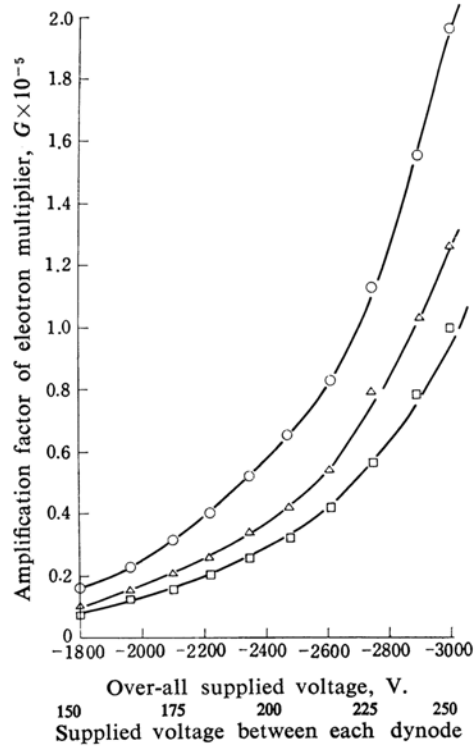

Fig. 7. Amplification factor of the electron multiplier tube constructed by the activated dynodes, as functions of supplied voltage to conversion dynode for inert gas ions. Circular, triangular and square points indicate the results for $^{4}He^{+}$, $^{20}Ne^{+}$ and $^{40}A^{+}$ ions, respectively.

figures, circles, triangles and squares indicate the results for helium 4, neon 20 and argon 40 ions respectively. The ions were accelerated by 1200 V. to earth potential during these measurements.

Discussion

The Influence of Ion Species on the Amplification Factor of the Secondary Electron Multiplier.—As may be seen from Figs. 6 and 7, the amplification factors of the electron multiplier are different for different ion species under the same conditions. In these results, the amplification factors of the ion currents were in the sequence, helium, neon and argon ions. In the results from the electro-polished dynodes, the ratios of the amplification factors are $He^+ : Ne^+ : A^+ = 2.45 : 1.79 : 1.00$ with each voltage. These ratios indicate that the amplification factors are roughly inversely proportional to the square root of the ion mass. This correlation obtained from the electro-polished dynodes agrees with the results obtained by Nier et al.[1] On the other hand, the ratios of the amplification factors obtained from the electron multiplier constructed with the activated dynodes are approximately $He^+ : Ne^+ : A^+ = 2.00 : 1.28 : 1.00$ for each voltage. These ratios indicate that the amplification factors have not the same correlation as the results from the electro-polished dynodes. These results indicate that the amplification factors vary according to the conditions of the treatment of the dynodes, a finding which is in agreement with the results obtained by Barnett et al.[12]

Average Yield of Secondary Electrons by Electron Bombardment. — The amplification factor of the electron multiplier, G, is given by the following relation:

$$G=\gamma_i \times \bar{\delta}^{n-1}$$

when γ_i is the ratio of the number of secondary electrons to positive ions at the conversion dynode, $\bar{\delta}$ is the average ratio of primary to secondary electrons on the succeeding dynodes, and n is the number of stages of the secondary-electron multiplier. γ_i is governed by the following factors: the chemical and physical natures of the dynode, the incident angle of the ions, the kinetic and potential energies of ions and ionic charge, etc., $\bar{\delta}$ is governed by the chemical and physical natures of the dynode, and the kinetic energy of the incident electrons. With regard to the results of this study, the kinetic energy of the ions bombarding the conversion dynode is the difference between the ion acceleration potential and the supplied voltage to the conversion dynode. Assuming that the ion energy dependency of the value γ_i is not varied in the ion energy above 1200 V. the value of γ_i can be obtained by the extrapolation of the data measured in a previous study[8]. The values of γ_i for ion energy obtained in the manner described above are shown in Tables I and II for the electro-polished and activated copper-beryllium dynodes. By using these γ_i values, the value of $\bar{\delta}$, the average yield of the secondary electrons at each electron energy, can be obtained; they are summarized in Tables I and II.

Influence of the Activation of Dynodes on the Amplification Factor of the Secondary Electron Multiplier.—For comparison of the electro-polished dynodes with the activated dynodes, the logarithms of the amplification factors are plotted as functions of the supplied voltage to the conversion dynode; they are shown in Fig. 8. In Fig. 8, the upper three curves are the results obtained from activated dynodes, while the lower three curves are the results obtained from electro-polished dynodes; the circles, triangles and squares indicate the helium, neon and argon ions respectively. As

Table I. Variation of $\bar{\delta}$ with electron energy and γ_i ($^{40}A^+$) with ion energy from electro-polished Cu-Be

Ion energy V.	γ_i Electrons / Ion	Electron energy V.	$\bar{\delta}$ Electrons / Electron
3050	2.65	154	1.47
3200	2.80	167	1.54
3350	2.95	179	1.58
3500	3.13	192	1.59
3650	3.28	204	1.65
3780	3.38	215	1.68
3910	3.53	226	1.69
4060	3.68	238	1.72
4200	3.80	250	1.74

Table II. Variation of $\bar{\delta}$ with electron energy and γ_i ($^{40}A^+$) with ion energy from activated Cu-Be

Ion energy V.	γ_i Electrons / Ion	Electron energy V.	$\bar{\delta}$ Electrons / Electron
3000	8.30	150	1.87
3160	8.75	163	1.92
3300	9.15	175	1.95
3440	9.50	186	1.99
3550	9.80	196	2.04
3680	10.1	207	2.07
3820	10.5	218	2.12
3940	10.8	228	2.18
4000	11.2	240	2.24
4200	11.5	250	2.29

is seen in Fig. 8, the amplification factors of the electron multiplier were radically increased by the activation of the dynodes, and the results show that the amplification factor increased almost exponentialy with the increasingly supplied voltage for all ions, while this was not so in the case of the electro-polished dynodes. When Tables I and II are compared, the values of γ_i and $\bar{\delta}$ show an increase as a result of the dynode activation. The voltage dependency of the amplification factor is mainly governed by the value of $\bar{\delta}$. From the value of $\bar{\delta}$ shown in Tables I and II, the difference in the energy dependency of the value $\bar{\delta}$ due to dynode activation is not clear, but from a comparison of the results in Fig. 8, the energy dependency of $\bar{\delta}$ is considered to be larger for the activated dynodes than for the electro-polished dynodes. In the previons studies[8-10], the increase in the secondary electron yield by activation of the copper-beryllium was explained by the contribution of the beryllium oxide formed near the surface, while for the ions having an energy higher than 1200 V. it was explained by the fact that the stopping power of the beryllium oxide is larger than that of the copper oxide. The increased values of $\bar{\delta}$ by dynode activation for electrons having an energy between 150 and 250 V. can be understood in the same way.

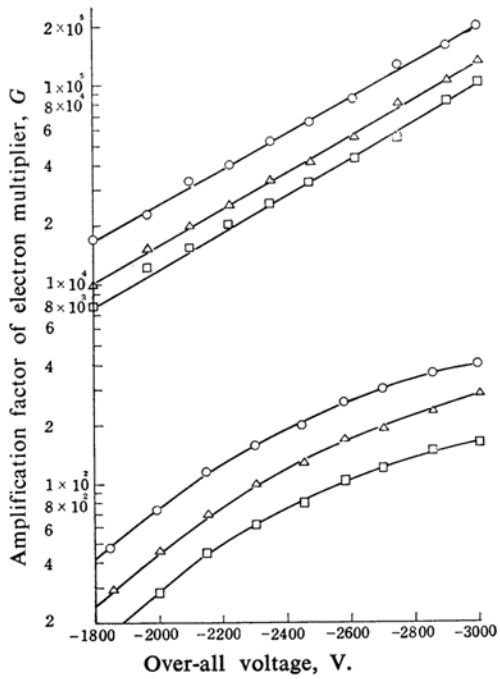

Fig. 8 Semilog plots of the amplification factor of the electron multiplier tube as a function of supplied voltage to conversion dynode for inert gas ions. Upper three curves are the results for activated dynodes, and lower three curves are the results for electro-polished dynodes, the signs of the curves are same as Figs. 6 and 7.

Summary

For the purpose of measuring very small ion currents by the mass spectrometer, a secondary electron multiplier, using the dynodes of copper-beryllium, has been constructed and installed. The amplification by the electron multiplier of various supplied voltages to the conversion dynode was measured for inert gas ions, and the amplification factor and its variation with the supplied voltage to the conversion dynode was compared with both the activated and the electro-polished dynode. For the electron multiplier using the electro-polished dynodes, the amplification was roughly inversely proportional to the square root of the ion mass, while for the activated dynode this was not the case. The average yield of the secondary electrons impacted by electrons on the copper-beryllium dynodes was determined, using the values of γ_i which had been estimated by extrapolation of the data obtained in a previous study. The increase of the amplification factors of the electron multiplier due to the dynode activation was explained on the basis of an increase in γ_i and $\bar{\delta}$ due to dynode activation, an increase to be attributed to the formation of beryllium oxide layers. In this study, an amplification factor of a 10^5 order for inert gas ions has been obtained with the electron multiplier constructed with dynodes made from activated copper-beryllium. By using this electron multiplier, ion currents of 10^{-19} amperes are easily detectable with a mass spectrometer using a conventional D. C. amplifier.

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