Oct. 28, 1969 TAMOTSU NODA ET AL 3,475,604

MASS SPECTROMETER HAVING MEANS FOR SIMULTANEOUSLY DETECTING SINGLE FOCUSSING AND DOUBLE FOCUSSING MASS SPECTRA

Filed Sept. 23, 1966 2 Sheets-Sheet 1

FIG. 1

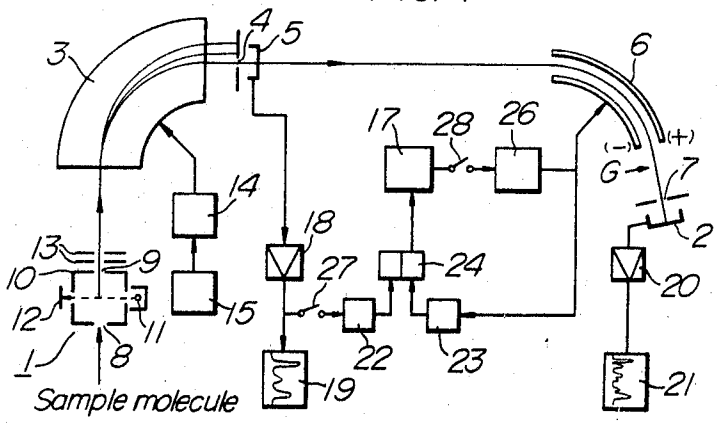
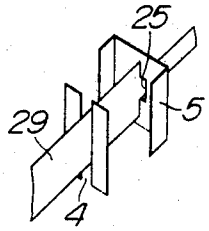


FIG. 2



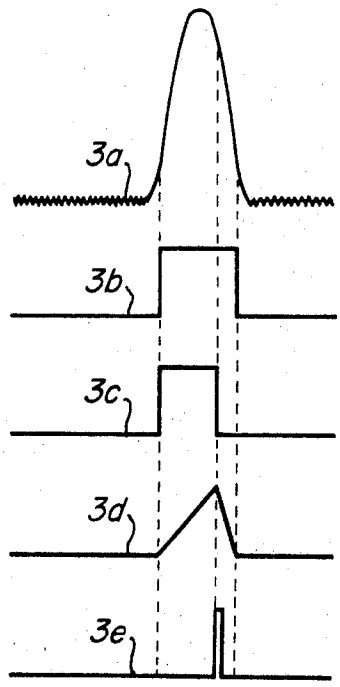


FIG. 3

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FIG. 4a

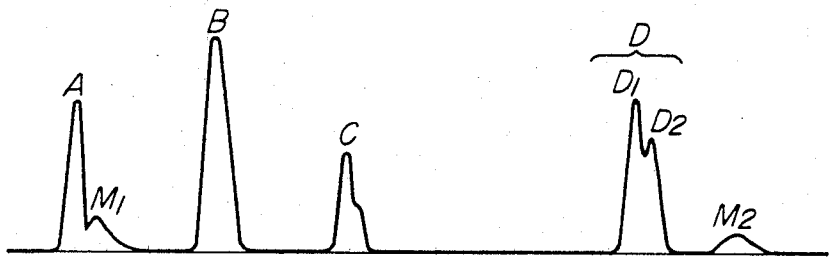


FIG. 4b

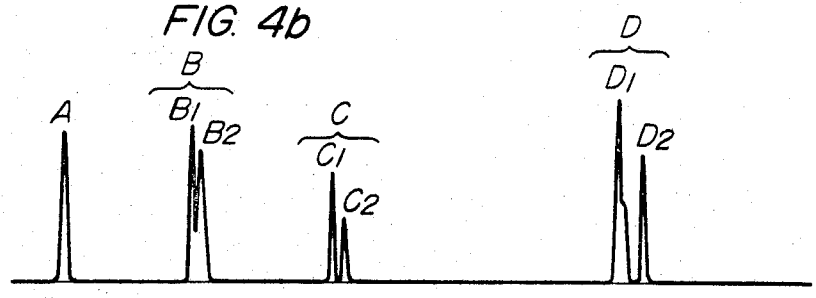
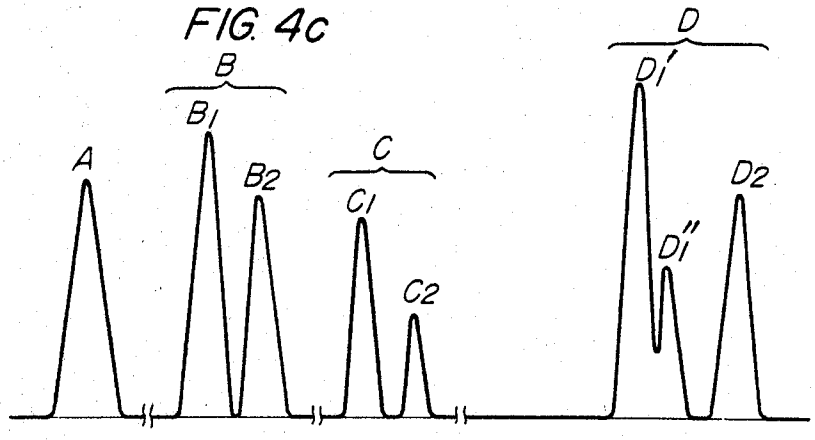


FIG. 4c



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MASS SPECTROMETER HAVING MEANS FOR SIMULTANEOUSLY DETECTING SINGLE FOCUSSING AND DOUBLE FOCUSSING MASS SPECTRA

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U.S. Cl. 250—41.9 4 Claims

ABSTRACT OF THE DISCLOSURE

A double focussing mass spectrometer in which ions produced by an ion source are dispersed by a magnetic field in accordance with the mass numbers thereof, the dispersed ions being successively detected by a first ion collector with a sweep of the magnetic field to provide a single focussing mass spectrum of low resolution including a large amount of metastable ions, while a part of the ions directed to the first ion collector is led to an electric field through the first ion collector without detection thereby to be dispersed in accordance with their velocity, ions having a specified velocity among the velocity dispersed ions being detected by a second ion collector to provide a double focussing mass spectrum of high resolution simultaneously with the single focussing mass spectrum.

This invention relates to mass spectrometers of the double focussing type.

It is commonly known that mass spectrometers of the double focussing type employing the combination of an electrostatic field and a magnetic field provide a mass spectrum of higher resolution than mass spectrometers of the single focussing type employing only a magnetic field therein. With due appreciation of the superiority of mass spectrometers of the double focussing type, it will be very advantageous if, in this type of mass spectrometer, it is possible to simultaneously obtain a double focussing mass spectrum (high-resolution mass spectrum) and a single focussing mass spectrum (low-resolution mass spectrum) resulting from sole use of a magnetic field, the latter spectrum including metastable ions in large amounts which have low and random energies. Provision of such a mass spectrometer of the double focussing type will be very advantageous because the structure of molecules can be analyzed easily, accurately and in full detail.

Accordingly, it is an object of the present invention to provide a mass spectrometer of the double focussing type which can simultaneously provide a double focussing mass spectrum and a single focussing mass spectrum including metastable ions in large amounts.

Another object of the present invention is to provide a mass spectrometer of the double focussing type which can provide mass spectra of improved sensitivity and resolution without a prolonged time for analysis as compared with mass spectrometers of the double focussing type commonly employed in the analysis of this sort.

The mass spectrometer of the double focussing type according to the present invention comprises, in the below-mentioned order, a series arrangement of elements including a source of ions, magnetic pole means for establishing a magnetic field and associated with means for effecting a sweep of the magnetic field, a first stage slit, a first stage ion collector, electrode means for establishing an electric field, a last stage slit and a last stage ion collector, and further providing means for simultaneously deriving electrical outputs from both the first stage ion collector and the last stage ion collector for recording the respective outputs independently of each other.

According to the mass spectrometer of the double focussing type of the invention having the configuration as described above, a double focussing mass spectrum appears on a recorder connected with the last stage ion collector, while a single-convergence mass spectrum including metastable ions therein appears on a recorder connected with the first stage ion collector.

The mass spectrometer of the double focussing type according to the present invention is further provided with means which is actuated each time an electrical output is derived from the first stage ion collector so as to utilize this electrical output for effecting a sweep of the electrostatic field established by the electrode until such time that this electrical output ceases to be derived. The sweep of the electrostatic field by the above means is effected to impart to an ion beam passing through the electrostatic field a brake action in a direction opposite to the direction of sweep of the magnetic field. The mass spectrometer of the double focussing type of the present invention having such electrostatic field sweep means can operate with an improved sensitivity and resolution without any prolonged time of analysis as compared with prior mass spectrometers of the double focussing type which are not equipped with electrostatic field sweep means of the nature as described above.

Other objects, advantages and features of the present invention will become apparent from the following description with reference to the accompanying drawings, in which:

FIG. 1 is a block diagram of the mass spectrometer of the double focussing type embodying the present invention;

FIG. 2 is a schematic perspective view showing positions of a first stage slit and a first stage ion collector relative to an ion beam;

FIG. 3 is a graphic illustration of output waveforms from various electric circuits in the mass spectrometer shown in FIG. 1; and

FIG. 4 is a graphic illustration of mass spectra for the purpose of explaining the marked effect attained by the present invention.

Referring to FIG. 1, the mass spectrometer of the double focussing type embodying the present invention includes an ion source **1** and a last stage ion collector **2** between which magnetic poles **3**, a first stage slit **4**, a first stage ion collector **5**, electrodes **6**, and a last stage slit **7** are disposed in the above order. The ion source **1** consists of an ionization chamber **10** having a sample introducing opening **8** and an ion emitting slit **9**, an electron source **11** for ionizing by electron bombardment the sample molecule coming into the ionization chamber **10** through the sample introducing opening **8**, an electron collecting electrode **12**, and an ion accelerating electrode system **13** for accelerating an ion beam emitting from the ion emitted slit **9**. The magnetic poles **3** are connected with a power supply **14** and a magnetic field sweep circuit **15**, while the electrodes **6** are connected with a power supply **26** and an electrostatic field sweep circuit **17**. An amplifier **18** and a recorder **19** are connected with the first stage ion collector **5**, while an amplifier **20** and a recorder **21** are likewise connected with the last stage ion collector **2**. A peak senser **22** is connected through a switch **27** with the output of the amplifier **18**, and an upper-limit discriminator **23** is connected with the power supply **26** from the output of the electrostatic field sweep circuit **17**. The outputs of the peak sensor **22** and the

upper-limit discriminator **23** are connected with a flip-flop circuit **24** whose output is connected with the electrostatic field sweep circuit **17**. Reference numerals **27** and **28** designate switches.

FIG. 2 shows the relation between the first stage slit **4** and the first stage ion collector **5** with respect to an ion beam **29**. A slit **25** is provided centrally of the first stage ion collector **5** to allow passage therethrough of a portion of the ion beam **29** having passed through the first stage slit **4**.

In the mass spectrometer having the structure as described above, a sample admitted into the ionization chamber **10** is ionized by being bombarded by electrons emitted from the electron source **11**, and the ionized ions are led out of the ionization chamber **10** through the ion emitting slit **9** and are accelerated by the accelerating electrode system **13** to be projected into the magnetic field. When, therefore, the power supply **14** for the magnetic field is energized and the magnetic field sweep circuit **15** is placed in operation to sweep the magnetic field established by the magnetic poles **3**, the ion beam introduced into the magnetic field is dispersed and deflected depending mainly on the difference of mass of ions to be successively collected through the first stage slit **4** on the first stage ion collector **5**. The collected ion beam on the first stage ion collector **5** is converted into an electric current which is then amplified by the amplifier **18** and applied to the recorder **19**. Thus, a mass spectrum is depicted on the recorder **19**.

On the other hand, a portion of the ion beam having passed through the first stage slit **4** passes through the slit **25** of the first stage ion collector **5** to be introduced into the electrostatic field established by the electrodes **6**. When, therefore, the power supply **26** is energized, the ion beam introduced into the electrostatic field is dispersed depending mainly on the difference of velocity of the ions and the dispersed ion beam is finally collected through the last stage slit **7** on the last stage ion collector **2**. The collected ion beam on the last stage ion collector **2** is converted into an electrical current which is then amplified by the amplifier **20** and applied to the recorder **21**. Thus, a mass spectrum is given on the recorder **21**.

In the above operation, the electrostatic field established by the electrodes **6** imparts to the ion beam a dispersing action due to the difference in the velocity of the ions and any deviation of the ion beam trajectory due to the difference in the velocity of ions is cancelled out by the mass dispersion due to the magnetic field. As a result, the mass spectrum appearing at the recorder **21** is of more high resolution than that at the recorder **19**. In other words, it may be said that a low-resolution mass spectrum (single-focussing mass spectrum) appears at the recorder **19** and a high-resolution mass spectrum (double focussing mass spectrum) appears at the recorder **21**.

Suppose now that a mass spectrum as shown in FIG. *4a* appears at the recorder **19** and its peaks B, C and D, for example, are multiplets. Then a mass spectrum that appears at the recorder **21** will have a form as shown in FIG. *4b* in which it will be seen that the former peaks B, C and D are clearly separated into peak components, B_1, and B_2, C_1 and C_2, and D_1 and D_2, respectively. In some cases, ions which are obtained as a result of the ionization of the sample molecule in the ion source **1** may be imparted with extra energy, and during their flight toward the first stage ion collector **5** from the ion source **1**, may decompose into light ions. These ions are generally called the metastable ions. When the metastable ions produced before the entrance of the ions into the magnetic field after their emergence from the ion source **1** are introduced into the magnetic field, they are deflected depending on the strength of the magnetic field. But, a sweep of the magnetic field will cause such action that those metastable ions corresponding to a certain field strength are solely collected through the first stage slit **4** on the first stage ion collector **5**. Peaks M_1 and M_2 in FIG. *4a* represent such metastable ions. Since, however, the metastable ions not only have random energies but also their energy levels are comparatively lower than those of common ions, they are heavily deflected during their passage through the electrostatic field and deviate from the expected ion trajectory with the result that they can not reach the last stage ion collector **2** and their peaks hardly appear at the recorder **21**.

The operation of the mass spectrometer with the switches **27** and **28** in their closed position will next be described. Suppose now the output of the amplifier **18** has a waveform as shown in line *3a* of FIG. 3. Upon detecting the emergence of such output, the peak senser **22** is actuated and gives an output waveform as shown in line *3b*. Simultaneously with the operation of the peak senser **22**, the flip-flop circuit **24** is set to develop an output waveform as shown in line *3c* and the electric field sweep circuit **17** is set in turn to develop an output waveform as shown in line *3d*. Thus the electric field sweep circuit **17** effects a voltage sweep ranging from an arbitrary reset voltage to an arbitrary upper-limit voltage, and the electric field established by the electrode **6** is thereby swept in such a manner that a brake action is imparted to the passing ion beam in a direction G in FIG. 1, which is opposite to the direction of sweep of the magnetic field. When the above voltage sweep reaches its upper limit, the upper-limit discriminator **23** is actuated and develops an output waveform as shown in line *3e*, this output acting to reset both the flip-flop circuit **24** and the electrostatic field sweep circuit **17**.

By the above manner of sweep of the electrostatic field, the transverse velocity of the ion beam passing through the electrostatic field is rendered small. Suppose that the mass spectrum of FIG. *4b* has been recorded beyond the limit of response of the amplifier **20**, then a mass spectrum appearing at the recorder **21**, as a result of the above manner of sweep of the electrostatic field, will be as shown in FIG. *4c* in which it will be seen that peaks are more distinctly separated than in the case of FIG. *4b*. The peak D in FIG. *4c* is shown as separated into three peak components D_1', D_1'' and D_2, and this proves the fact that the peak D_1 in FIG. *4b* is separated into two peak components D_1' and D_1'' by the effect of the sweep of the electrostatic field as described above. Further, since the above manner of sweep of the electrostatic field is effective to increase the number of ions per unit time detected at the last stage ion collector **2**, the mass spectrum of FIG. *4c* is of higher sensitivity than the mass spectrum of FIG. *4b*.

It may be considered advantageous to make a slow sweep of the magnetic field, in order to obtain an improved sensitivity and resolution, but this is undesirable in view of an extended time of analysis. According to the invention, however, the sweep of the electrostatic field is carried out within a limited time ranging from the first appearance of an output signal from the first stage ion collector **5** to the termination of such output signal. The mass spectrometer of the double focussing type according to the invention is extremely advantageous over conventional mass spectrometers of the double focussing type having no provision of electrostatic field sweep means in that it gives mass spectra of improved sensitivity and resolution without any prolonged time of analysis.

What we claim is:

1. A mass spectrometer of the double focussing type comprising, arranged in the following order, an ion source, magnetic pole means for establishing a magnetic field, magnetic sweep means associated with said magnetic pole means for effecting a sweep of the magnetic field, a first stage slit, a first stage ion collector, electrode means for establishing an electrostatic field, a last stage slit and a last stage ion collector, and means for simultaneously deriving electrical outputs from both said first stage ion collector and last stage ion collector for recording the respective outputs independently of each other.

2. A mass spectrometer of the double focussing type according to claim 1, comprising electrostatic sweep means actuatable each time an electrical output is derived from said first stage ion collector so as to utilize this electrical output for effecting a sweep of the electrostatic field until such time that this electrical output ceases to be derived, the sweep of the electric field by said means being effected to impart to an ion beam passing through the electrostatic field a brake action in a direction opposite to the direction of sweep of the magnetic field.

3. A mass spectrometer of the double focussing type according to claim 2, wherein said electrostatic field sweep means comprises a peak senser for detecting the output of said first stage ion collector, a flip-flop circuit urged to its set position by said peak senser, an electric field sweep circuit urged to its set position in response

to the setting of said flip-flop circuit, and an upper-limit discriminator operative to detect the upper limit of sweep by said electrostatic field sweep circuit for thereby urging said flip-flop circuit and said electric field sweep circuit to their reset positions.

4. A mass spectrometer according to claim 1, wherein said first stage slit passes ions having substantially the same mass therethrough to said first stage ion collector.

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