

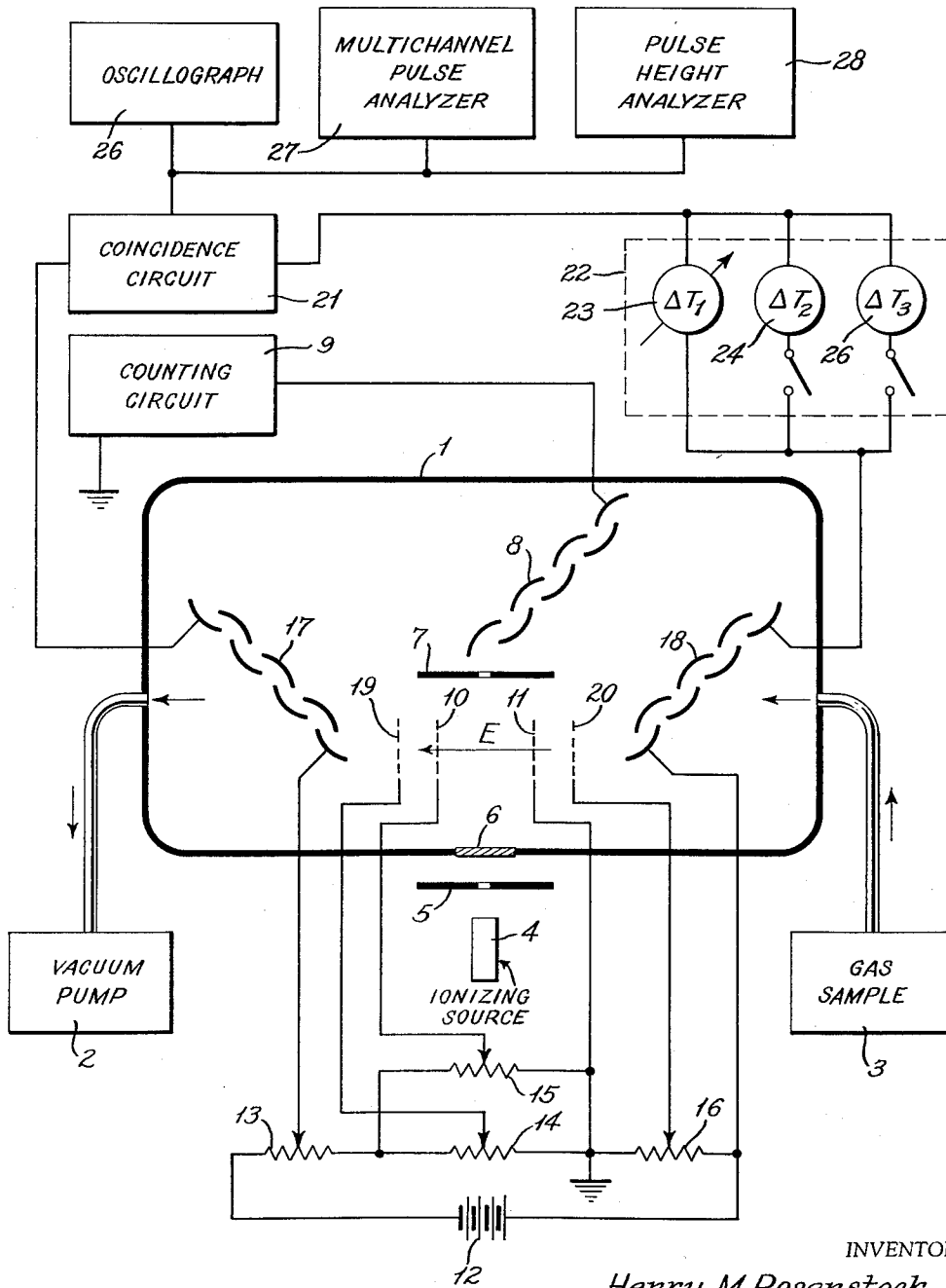
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METHOD AND APPARATUS FOR IONIZATION INVESTIGATION

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METHOD AND APPARATUS FOR IONIZATION INVESTIGATION

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This invention relates to investigation of ionization phenomena, and more particularly to an improved method and apparatus especially designed for mass spectroscopy.

Previously designed apparatus for mass spectroscopy has not been capable of studying each ionization event, though it is highly desirable to be able to study the exact physical process which takes place when an ionizing particle strikes and ionizes an atom. The method and apparatus of this invention relies upon a different principle than that involved in conventional mass spectroscopy and is capable of detecting and allowing the study of single ionization events.

Conventional mass spectrometers are generally divided into two different classes. One class relies upon a difference in deflection of ions subjected to an electric or magnetic field, or combination of such fields, depending upon the masses of the different ions. A more recent development in the mass spectroscopy field is the use of the different time-of-flight between ions of different masses, when the ions are subjected to an electric field. However, neither of these classes of spectroscopes have enabled the study of single ionization events. Moreover, these prior art spectroscopes have required an ionizing beam source of high intensity in order to furnish an output which is detectably higher than the noise generated in the usual ion detectors.

The apparatus of the present invention, on the other hand, permits the use of a radioactive source, as well as of sources conventional with known mass spectrometers. The invention relies upon the time-of-flight principle, but rather than detecting the difference in times-of-flight of positive ions of different masses, the present invention utilizes the difference in time-of-flight of the positive ions and electrons of any particular ion-pair. In other words, the invention depends upon the fact that an ion-pair which is subjected to an electric field will have its positive ions and electrons accelerated to different velocities because the electrons are of extremely small mass as compared with the positive ions. Further, the positive ions of different masses will attain velocities inversely proportional to their masses, while the electrons, being all of the same mass, will reach the same velocity, with constant field intensity.

The principles above discussed are utilized by subjecting a sample to be investigated to an ionizing beam, which may be a radioactive source, then subjecting the resultant ions formed by the beam striking the sample to an electric field which urges the positive ions and electrons of each ion-pair, corresponding to each ionization event, in different directions. The positive ions and electrons are then detected and the difference in velocity of the positive ions and electrons of an ion-pair used as an indication of the mass of the particular ion. Specifically, the output of the electron detector is subjected to a time delay corresponding to the difference in arrival times thereof of the positive ions and electrons of an ion-pair of selected mass, and the delayed electrons are compared with the positive ions for coincidence in time, such coincidence indicating the creation of an ion-pair of mass corresponding to the particular time delay.

The number of coincidences obtained by the apparatus may then be counted and the time-of-flight changed by

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adjustment of the electric field intensity, or the time delay changed, to cause coincidences corresponding to different mass numbers. The number of coincidences of each mass will be an indication of the number of ionization events of elements corresponding to that mass, so that comparison of the outputs for various times-of-flight or time delays will furnish an indication of the proportion of elements of various masses present or formed in the sample under investigation.

The apparatus to be further disclosed hereinafter includes an ion-multiplier for each of the positive ions and electrons. The use of such multipliers is conventional in mass spectrometers, but only one such multiplier is normally employed, because only the positive ions are detected. At any rate, the ion multiplier generates a great deal of noise which has no relation to the ions which actually strike it. Thermionic emission, cosmic rays striking the detector, and other causes result in a noise voltage which is so high that the source in the conventional mass spectrometer must be of high intensity in order to permit the operator to distinguish between an output from the detector corresponding to an ion striking it and an output corresponding only to noise. In the method and apparatus of this invention, however, the use of the coincidence principle reduces the effect of the noise to such an extreme degree that it is possible to operate with an extremely low intensity ion source, and even a radioactive source.

The method and apparatus of the present invention will now be more fully described in conjunction with the drawing showing a preferred embodiment thereof.

In the drawing, the single figure is a schematic diagram of a preferred embodiment of the apparatus of the invention.

The apparatus of the invention includes a container 1 which is preferably evacuated by a vacuum pump 2 to a very low pressure, which in the usual gas analysis will be of the order of 10^{-5} mm. of mercury. Though the apparatus is equally capable of investigating ionization of a solid or liquid sample, the apparatus illustrated is shown for gas analysis and includes a gas container 3 from which the gas sample is bled into the evacuated container 1.

The ionizing beam used in the apparatus is obtained from an ionizing source 4 which may be a natural or artificial radioactive source such as polonium for alpha rays, a solid form beta-emitter, a gas discharge, an ultraviolet monochromator, a thermionic emitter of electrons, or an X-ray tube. The above are merely examples of various possible sources that could be used in the apparatus of the present invention.

The ionizing beam from source 4 is collimated by means such as a slit schematically indicated at 5 and directed through window 6 into the evacuated container. There the beam strikes the gas particles and causes ionization thereof in a well-known manner. The beam is then directed through a collector shield 7 onto a detector 8 of the electron multiplier type. The output of the detector 8 is connected to a counting circuit 9 for indicating the intensity of the ionizing beam. The shield 7, detector 8, and counting circuit 9 may be used to line up the beam to its desired direction, and it may also be used for another purpose to be discussed hereinafter.

The ion-pairs formed in the evacuated container 1 by the ionizing beam are subjected to an electric field having the direction indicated by the arrow and symbol E, by a pair of grids 10 and 11 extending parallel to the beam path and at opposite sides thereof. Grid 10 is provided with a positive potential through connection to a suitable source of electric potential indicated as battery 12. The series combination of potentiometers 13, 14, 15 and 16 is connected across the battery, with potentiometers 14

and 15 connected in parallel and the junction between them and potentiometer 16 connected to ground. The grid 11 is grounded.

With the electric field created by the voltage applied to the ion-pair drawout grids 10 and 11 and the voltage source, the positive ions are urged in the direction of the arrow, while the negative ions are urged in the opposite direction.

The positive and negative ions of each ion-pair are collected by appropriate detectors 17 and 18, respectively, shown as of the electron multiplier type. The positive ions are retarded or accelerated, depending upon the effect desired, by a grid 19 positioned parallel to grid 10 and between that grid and detector 17. Grid 19 is connected to potentiometer 14 so that grid 19 may be adjusted to either a negative or positive voltage with respect to grid 10, according to the relative adjustments of potentiometers 14 and 15.

The negative ions or electrons are accelerated by a grid 20 parallel to grid 11 and extending between that grid and negative ion detector 18. Grid 20 is connected to potentiometer 16 to obtain a positive voltage for accelerating the electrons toward the detector.

The output of the positive ion detector 17 consists of pulses of voltage of amplitudes corresponding to the number of positive ions that strikes the detector at any instant of time, and with time separation corresponding to the interval between impingements of positive ions on the detector. That output is connected to one input of a coincidence circuit 21 whose characteristics will be described hereinafter.

The output of the negative ion detector 18 is connected to a time delay circuit 22 which may include a plurality of parallel time delay networks 23, 24 and 25, all connected in parallel. The outputs of the time delay networks are connected to the other input of coincidence circuit 21. The input to the time delay circuit 22 is a series of voltage pulses of amplitudes corresponding to the numbers of electrons that strike detector 18 at any instant, and with time intervals between them corresponding to the time intervals between impingements of electrons on the detector. These voltage pulses are delayed in the time delay circuit by various selected amounts. For instance, time delay network 23 delays voltage pulses by an adjustable amount indicated as delta t_1 , while time delay networks 24 and 25 delay their inputs by intervals delta t_2 and delta t_3 . Networks 24 and 25 are shown as provided with switches 24' and 25' to enable their disconnection from the circuit.

Coincidence circuit 21 is of a conventional type well known in the art, which supplies a pulse of voltage whenever voltage pulses arrive at its two inputs simultaneously, but which does not supply such a pulse in the absence of simultaneous inputs. It is also preferable that the coincidence circuit yield an output voltage upon detection of a time coincidence which is of amplitude corresponding to the amplitude of at least one of the inputs. For instance, the coincidence circuit may be of the well-known type which provides an output pulse of amplitude proportional to the product of the amplitudes of its inputs.

The output of coincidence circuit 21 consists of pulses of voltage corresponding to the number and arrival times of coincidences at the inputs thereof. This output may be indicated by such devices as oscillograph 26, multi-channel pulse analyzer 27, and/or pulse height analyzer 28, all of well known and conventional type.

In operation of the apparatus described above, when an ion-pair is created within evacuated container 1 by the ionizing source 4, the electric field between the grids urges the negative ion or electron toward detector 18 and the positive ion toward detector 17. These ions arrive at the detectors at transit times after the creation of the ion-pair which depend upon their relative masses. The electron, being of extremely small mass in com-

parison with the positive ion, will arrive at detector 18 an appreciable time before the positive ion strikes detector 17. The detectors 17 and 18 are spaced apart with reference to the area of ionization a distance such that the different transit times for the positive and negative ions to these detectors is detectable by electrical circuits.

The electron from an ion-pair under study will strike detector 18 before the corresponding positive ion reaches detector 17. Each ion will create a pulse of voltage in the detector. The negative ion pulse will be delayed by an interval corresponding to the setting of the time delay circuit 22. If that setting is of the proper amount, the pulse of voltage from positive ion detector 17 will arrive at coincidence circuit 21 simultaneously with the delayed pulse of voltage corresponding to that generated by the electron impinging upon detector 18. The coincidence circuit will then furnish an output pulse which may be indicated by an oscillograph or another appropriate indicator. The amount of the time delay necessary to cause such coincidence will then be directly related to the mass of the ion created within container 1. If a number of positive ions strike detector 17 simultaneously, the resultant output voltage will be much greater than that corresponding to a single ion, and the coincidence circuit output will be a voltage of amplitude corresponding to the number of positive ions striking detector 17.

If only one of the time delay networks is in time delay circuit 22 at the time, and ionization of an element of different mass than that which creates a coincidence at circuit 21 takes place, the positive ion pulse will reach the coincidence circuit at a different time from the delayed negative ion pulse. The ion-pair therefore will not be detected. The delay network 23, however, may be adjusted to furnish a time delay appropriate for this particular ion mass, in which event the coincidence circuit will count ion-pairs of that mass and discriminate against ion-pairs of any other mass.

It will be apparent from the above that the apparatus described responds to each ionization event, rather than to all ions striking a detector at a particular instant of time, irrespective of the ionization events from which these ions result. The latter is a feature of the conventional time-of-flight mass spectrometer, and the single event detection feature clearly distinguishes the apparatus of this invention therefrom.

The different time delay networks 23, 24 and 25, may be set to correspond to differing transit times indicative of different mass ionization events. For instance, if acetylene gas is being studied, sufficient time delays could be provided to correspond to mass numbers 26, 25, 24, 12, 2 and 1. The oscillograph or other indicator would thereupon indicate the presence or absence of atoms and molecules of these particular mass numbers, and the relative amplitudes of the indications would furnish a direct indication of the relative proportions of those mass numbers. The apparatus could therefore function as an isotope assay tool.

Another possible use of the apparatus is for the fundamental study of the effects of alpha particles, X-rays, high energy electrons, or heavy ions on gases. A particular gas under study could be bled into the container 1 and subjected to a beam from an appropriate source 4 of such particles or rays. The resulting ionizations would cause the positive ions and electrons of the ion-pairs to reach the respective detectors 17 and 18 at relative times which may be calculated from a knowledge of the electric field gradient and a knowledge of the possible ions that could be formed by such a beam. The coincidence spectrum could then be searched, either by varying the delay time of time delay network 23, or varying the field gradient by adjusting the various potentiometers 13-16. The relative numbers of the various coincidences would then be proportional to the relative numbers of different mass ions formed in the ionization events. This study would be expected to yield

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a more detailed knowledge of the precise details of the ionization events than is possible with presently-known apparatus.

It has been indicated above that a variation in velocity and hence transit time may be used, rather than a variation in time delay, to provide for coincidences. Such variation, as indicated, may be obtained by adjustment of the several potentiometers, the potentiometer settings or voltage amplitudes being an indication of the mass numbers in the event of coincidences at circuit 21.

It was also indicated above that a solid or liquid sample could be investigated with the present apparatus, rather than the gas sample provided for by the illustrated apparatus. Such samples could be positioned in the vicinity of the ionizing beam and vaporized, or the solid sample could be placed directly in the path of the ionizing beam.

It has been mentioned hereinabove that the indication of the intensity of the ionizing beam obtained from counting circuit 9 could be used for a purpose other than the mere alignment of the beam source. An instance of such other use is the determination of the ionization cross-section of the sample under study. Such a determination requires a knowledge of the intensity of the ionized beam, which could be obtained from counting circuit 9, the gas pressure in the container 1, which could be obtained from an appropriate pressure meter (not shown) and the number of ionizations per unit of time. The latter information is obviously supplied by the apparatus shown. The ionization cross-section of the gas under study could therefore readily be calculated.

It is also possible with the apparatus described to study the phenomenon of formation of doubly-charged ions. Such ions could be distinguished from singly-charged ions by the pulse height analyzer 28 and, for instance, the relative numbers of ionization events which create doubly-charged ions determined. Another possibility for distinguishing between doubly-charged and singly-charged ions may be the resolution of a double pulse at the electron collector due to the electrons from one ionization event. Such double pulses might be created if the initial velocities of the electrons from the doubly-charged ions were directed in different directions with respect to the negative ion collector, thus causing a time difference in arrival of the electrons at the negative ion detector.

It is further possible with this apparatus to study and distinguish between the formation of primary and secondary ion-pairs, since this apparatus examines each ionization event separately.

In order to provide for very extreme accuracy of the results it might be desirable to enclose the ionization region in a separate container so that it might operate at a higher gas pressure than obtains in the region of the ion detectors.

It will be evident that the method and apparatus above described are based upon a fundamentally new method of ionization investigation. It is therefore apparent that many minor changes could be made in both the method and the apparatus without departure from the scope of the invention. The invention therefore is not to be considered limited to the description above and the embodiment shown in the drawing, but rather only by the scope of the appended claims.

The above explanation has been predicated on the creation of only electrons as negative ions in each ion-pair. It is of course possible that, under appropriate conditions, the ion-pair will consist of a positive ion and a negative ion which is not an electron. However, this ionization process is generally a resonance phenomenon which is important only for a small energy range of the ionizing radiation. Such ionization process occurs at absolute energies which are less than the ionizing potential, less than 15 electron volts. With relatively high

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energy particles, such as alpha particles in the million electron volt range, the possibility of such a resonance phenomenon occurring is negligibly small. However, the phenomenon itself could be studied if a very low energy source, such as ultraviolet light were used. The delay times for coincidences in this type of investigation would give only the mass ratios of two ions but such ratios could be very useful.

It will be appreciated that if the ionizing beam consists of charged particles, they will be deflected by the electric field between the grids. However, for particles in the kev. range or higher, the magnitude of the field between the grids, since the voltage source connected thereto will be only a few volts in potential, will not cause enough deflection to interfere with the detection of ion-pairs. If a source of, say, 15 volts electrons were used, however, the apparatus would not respond in the indicated manner.

It will be evident from the above explanation that it would be possible to calculate the absolute masses of particular ions, but a much simpler procedure is to calibrate the apparatus with a standard sample of known mass and composition and then to obtain the relative masses and proportions of a sample based on the results with the standard.

I claim:

1. The method of investigating an ionization process which comprises directing an ionizing beam upon a sample to ionize atoms thereof, subjecting the resultant ion-pairs to an electric field to urge the positive and negative ions in different directions, and detecting the positive and negative ions of each ion-pair of ionized atoms of a predetermined mass in accordance with the difference in velocities caused by the difference in mass of the positive and negative ions.

2. The method of investigating an ionization process which comprises directing an ionizing beam upon a sample to ionize atoms thereof, subjecting the resultant ion-pairs to an electrostatic field of predetermined intensity to urge the positive and negative ions of each ion-pair in different directions to detectors of predetermined distance therefrom, and determining which ion-pairs correspond to an element of selected mass from the difference in transit time of the positive and negative ions of ion-pairs of that mass to such detectors.

3. The method of claim 2 including the step of detecting the number of ion-pairs of said element to obtain an indication of the portion of atoms of said selected mass in said sample.

4. The method of determining the presence of an element of a particular mass in a sample which comprises subjecting the sample to an ionizing beam, subjecting the resultant ions to an electric field to urge negative and positive ions in different directions, detecting the negative and positive ions separately at distances from the ionization area, and detecting the presence of an ion-pair of such particular mass by the difference in velocities of the positive and negative ions.

5. The method of ionization investigation which comprises subjecting a sample to an ionizing beam, subjecting the resultant ions to an electrostatic field to urge negative and positive ions in different directions, detecting the negative and positive ions separately at distances from the ionization area, delaying the response from the negative ions to effect a time coincidence between the negative and positive ions, and identifying the mass of the ion-pairs by the magnitude of such delay.

6. The method of mass spectroscopy which comprises directing an ionizing beam upon a sample to be analyzed to ionize atoms thereof, subjecting the resultant ion-pairs to an electrostatic field to urge the positive and negative ions in different directions, detecting the positive and negative ions at positions spaced from the ionization area, delaying responses from negative ions obtained at the detector by the time interval corresponding to the difference

in transit time of the negative and positive ions of each ion-pair of one particular mass, and indicating the number of time coincidences between arrival of positive ions at the detector and the delayed negative ion responses.

7. The method of claim 6 which includes the step of varying the delay time interval to obtain time delays corresponding to the different transit times of positive and negative ions of ion-pairs of different mass elements and indicating the time coincidences at each such time interval to obtain the relative proportions of such different-mass elements in the sample.

8. The method of claim 6 including the step of detecting the intensity of the ionizing beam, whereby the ionization cross-section of the sample can be calculated.

9. The method of claim 6 including the steps of varying the electrostatic field intensity to correspondingly vary the transit times to cause coincidences corresponding to ion-pairs of different masses, and indicating the time coincidence at each such field intensity to obtain the relative proportions of such different-mass elements in the sample.

10. Apparatus for studying the ionization of a sample which comprises an ionizing beam source operable to direct its beam upon said sample, means forming an electric field adjacent the area of ionization for urging the positive and negative ions of each ion-pair in different directions away from said area and means for furnishing a response to formation of ions of a particular mass from the difference in velocities of the positive and negative ions of the ion-pairs of that mass.

11. Apparatus for studying the ionization of a sample which comprises a source of an ionizing beam oriented to direct such beam onto the sample, means forming an electric field adjacent the area of ionization for urging the positive and negative ions of each ion-pair in different directions away from such area, positive and negative ion detectors positioned in the path of such positive and negative ions, respectively, at distances from the area of ionization, and means connected to said detectors responsive to the different transit times of the positive and negative ions of ion-pairs of a particular mass for furnishing a response to formation of ions of that mass.

12. Apparatus for studying the ionization of a sample which comprises a source of an ionizing beam oriented to direct such beam onto the sample, means forming an electric field adjacent the area of ionization for urging the positive and negative ions of each ion-pair in different directions away from such area, positive and negative ion detectors positioned in the path of such positive and negative ions, respectively, at distances from the area of ionization, coincidence means for detecting the number of time coincidences between voltage pulses reaching it at a pair of inputs, said detectors being operable to translate each ion arrival thereat into a pulse of voltage, means connecting the positive ion detector to one input of said coincidence means, and time delay means connected between the negative ion detector and said coincidence means for delaying the detector output pulses by a predetermined time interval corresponding to the difference in transit time of the positive and negative ions of an ion-pair of a preselected mass from the area of ionization to the respective detectors.

13. The apparatus of claim 12 including means for adjusting the arrival time of pulses from the negative ion detector at said coincidence means to permit determination of coincidences corresponding to different-mass ions.

14. The apparatus of claim 13 in which said adjusting means includes means for varying the intensity of said electric field.

15. The apparatus of claim 13 in which said adjusting means includes means for adjusting the time delay means to delay pulses from the negative ion detector by different time periods.

16. The apparatus of claim 12 in which said time delay means includes a plurality of delay circuits of different delay times connected in parallel, and an oscillograph con-

nected to the output of said coincidence means for exhibiting the relative proportions of ions of different masses corresponding to said different delay times.

17. The apparatus of claim 12 in which each of said detectors is an ion-multiplier.

18. The apparatus of claim 12 in which said source is a radioactive source.

19. A coincidence mass spectrometer including a source of an ionizing beam oriented to direct such beam onto a sample to be examined, means forming an electrostatic field adjacent the area of ionization for urging the positive and negative ions of each ion-pair in different directions away from such area, positive and negative ion-multipliers positioned in the paths of such positive and negative ions, respectively, at distances from the area of ionization sufficient to allow the differing velocities of the positive and negative ions to cause impingements upon their respective detectors at detectably different times, a coincidence circuit operable to furnish an output pulse of magnitude proportional to at least one of its input pulses when a pair of pulses arrives simultaneously at its pair of inputs, the output of the positive ion multiplier being connected directly to one input of the coincidence circuit, time delay means connected between the negative ion-multiplier and the coincidence circuit operable to delay voltage pulses for a time period corresponding to the difference in arrival time of the positive and negative ions of an ion-pair at their respective ion-multipliers, and means connected to the output of said coincidence circuit for indicating the amplitude of the output voltage thereof.

20. The apparatus of claim 19 including means for adjusting the magnitude of the electrostatic field intensity to vary the difference in arrival time of the positive and negative ions of an ion-pair at their respective ion-multipliers, thereby to cause output pulses from the coincidence circuit to correspond to ions of different masses.

21. The apparatus of claim 19 in which said time delay means is adjustable to vary the time delay thereof to cause output pulses from the coincidence circuit to correspond to ions of different masses.

22. The apparatus of claim 19 in which said time delay means includes a plurality of parallel-connected time delay circuits operable to delay pulses from the negative ion-multiplier by different time periods corresponding to ions of different masses.

23. The apparatus of claim 22 in which said indicating means is an oscillograph.

24. The apparatus of claim 22 in which indicating means is a multichannel pulse analyzer.

25. The apparatus of claim 22 in which said indicating means is a pulse height analyzer.

26. The apparatus of claim 22 in which said source is a radioactive source.

27. The apparatus of claim 26 in which said radioactive source supplies an ionizing beam of alpha particles.

28. The apparatus of claim 19 in which said electrostatic field-forming means includes a pair of grids positioned adjacent the area of ion formation and a voltage source connected between the grids.

29. The apparatus of claim 28 including a second pair of grids positioned at opposite sides of said first-mentioned grids and connected to said voltage source to accelerate the positive and negative ions toward their respective detectors.

30. The apparatus of claim 19 including a counting detector in the path of said ionizing beam to detect the intensity thereof, whereby the sample cross-section may be calculated.

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