United States Patent [19]

Roehrig et al.

[11] **3,835,319**

[45] **Sept. 10, 1974**

[54] **COLD CATHODE ION SOURCE MASS SPECTROMETER WITH STRAIGHT LINE ARRANGEMENT OF ION SOURCE AND ANALYZER**

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[73] Assignee: **National Research Corporation,** Cambridge, Mass.

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 811,139, March 27, 1969, abandoned.

[52] **U.S. Cl.** **250/290,** 250/423, 313/359, 313/231

[51] **Int. Cl.** **H01j 39/34**

[58] **Field of Search** . 250/41.9 G, 41.9 SB, 41.9 SE, 250/41.9 DS; 313/7, 63, 230, 231; 324/33

[56] **References Cited**

UNITED STATES PATENTS

3,051,868	8/1962	Redhead	324/33 X
3,075,976	1/1963	Gunther	250/41.9
3,378,712	4/1968	Lafferty	313/7

OTHER PUBLICATIONS

"Cold Cathode Quadrupole Mass Spectrometer" by P. Blum, et al., from The Review of Scientific Instruments, Vol. 38, No. 10, Oct., 1967, pages 1404–1408.

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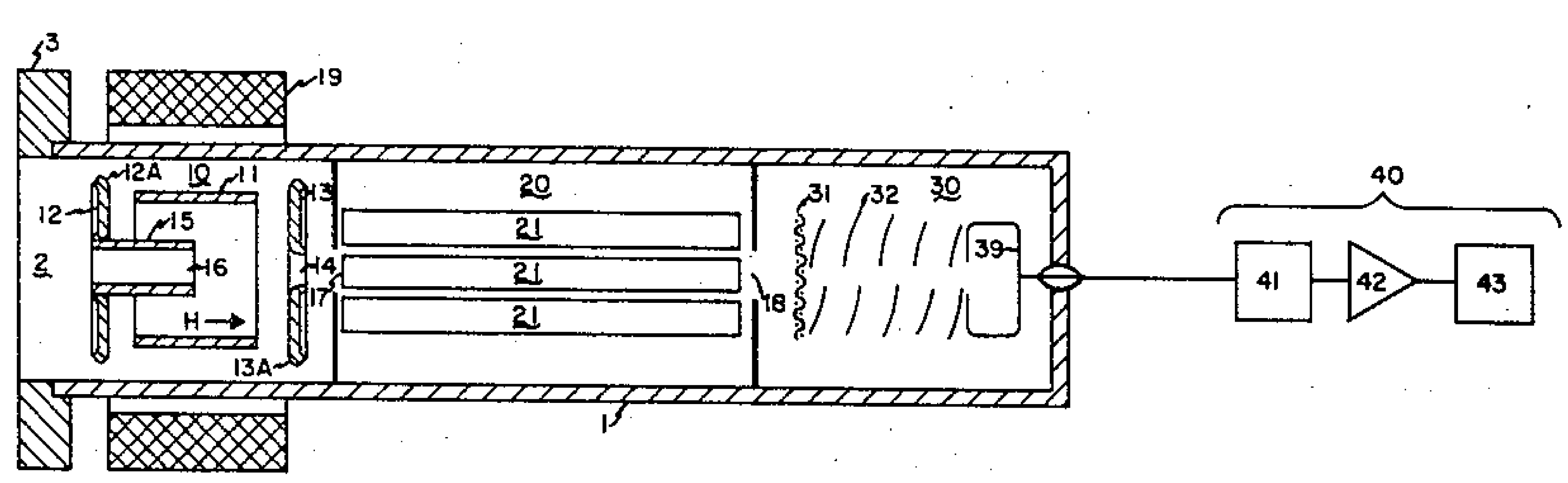
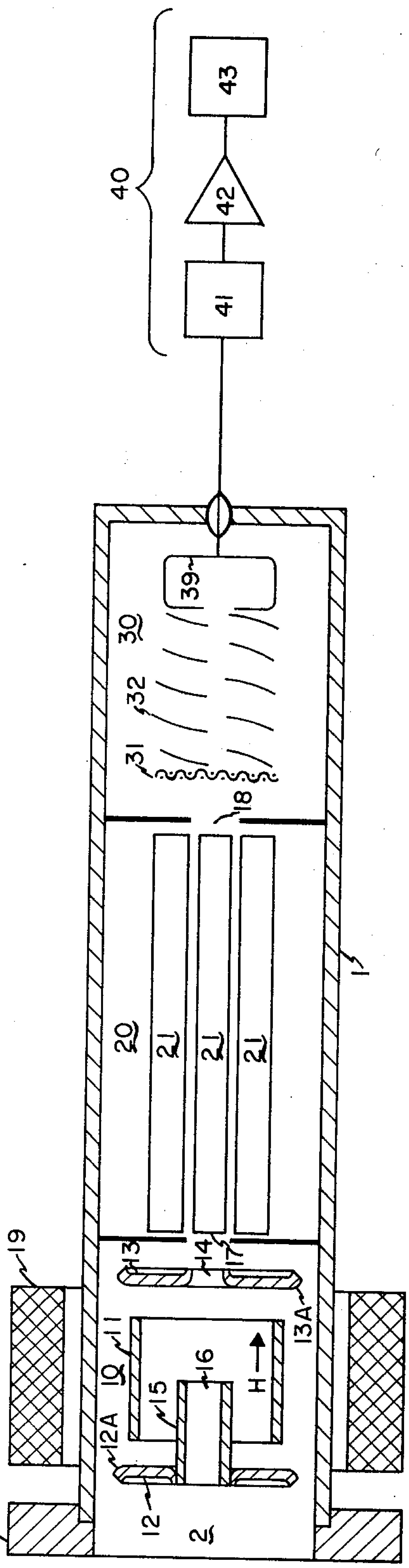
[57] **ABSTRACT**

Mass spectrometer combination and ion source subcombination therefor. The mass spectrometer has a magnetron ion source, a quadrupole ion analyzer and an ion collector with digital counting read-out and this is useful for residual gas analysis, partial pressure analysis and chemical composition determination and is particularly suited for ultra-high vacuum usage yielding high sensitivity and improved signal-to-noise ratio, consistent with low weight and bulk. The ion source is constructed so that photons are not produced at those loci which can be viewed through the ion exit aperture thereof. Thus, the spectrometer collector is free from impingement thereon of light energy and the signal-to-noise ratio of the instrument is improved thereby.

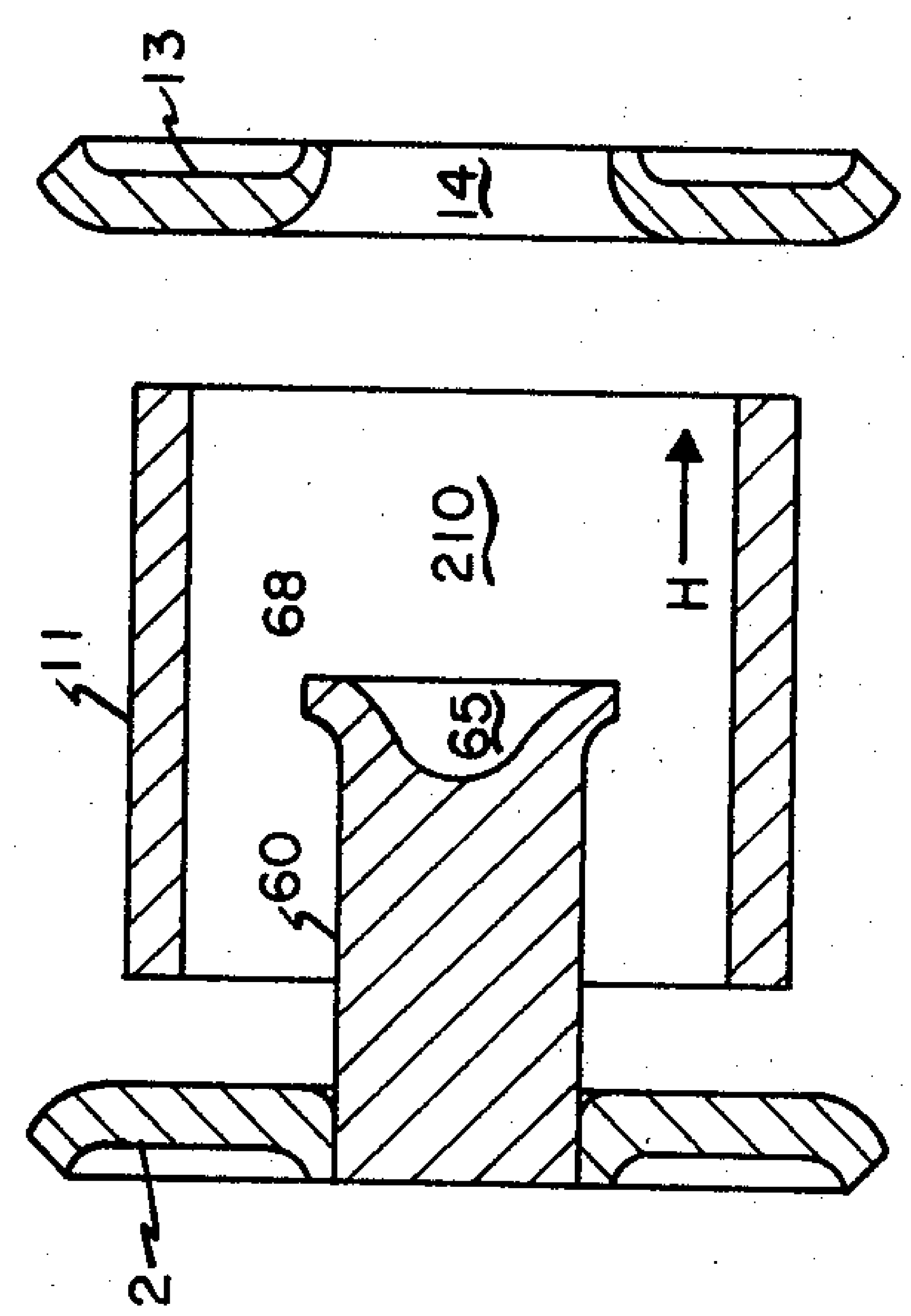
9 Claims, 2 Drawing Figures





40
41
42
43
39
30
32
31
18
20
21
21
21
1
19
13
14
17
13A
11
10
16
15
12A
H
12
2
3

FIG. 1



13
14
11
68
210
H
65
60
12

FIG. 2

COLD CATHODE ION SOURCE MASS SPECTROMETER WITH STRAIGHT LINE ARRANGEMENT OF ION SOURCE AND ANALYZER

CROSS-REFERENCE

This application is a continuation-in-part of our copending U.S. Serial No. 811,139, filed Mar. 27, 1969 now abandoned.

The invention described herein was made in the performance of work under a NASA contract and is subject to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 U.S.C. 2457).

FIELD OF THE INVENTION

The present invention relates to mass spectrometer instruments and comprises an improvement in such instrumentation particularly suitable for residual gas analysis in vacuum pumped systems and partial pressure analysis. It may also be used for chemical composition analysis in combination with conventional means for converting a solid or liquid sample to a gas sample and feeding it to the spectrometer.

The invention is especially useful for, and distinctly advantageous in connection with operations under high vacuum (10^{-4} mm. Hg. range and below) and specifically comprises an improved mass spectrometer combination and improved ion source subcombination therefor, the spectrometer being of the type which provides a cold cathode ion source in straight line alignment with a non-magnetic analyzer such as one of the quadrupole type.

BACKGROUND OF THE INVENTION

Cold cathode ion sources are well known, e.g., U.S. Pat. Nos. 2,499,289; 2,636,990; 3,075,076; 3,117,224; and 3,287,589. Such sources are essentially derived from the Penning Ion Gauge, U.S. Pat. No. 2,146,025 and U.S. Pat. No. 2,197,079. The advantages of cold cathode ion sources over hot cathode sources are summarized in Blum and Torney, "Cold Cathode Quadrupole Mass Spectrometer," Review of Scientific Instruments, Vol. 38 No. 10, 1404–1408 (October 1967). This last cited article also sets out recent state of the art in connection with the development of a mass spectrometer comprising a cold cathode magnetron ion source (which source is a modification of the Redhead ion gauge, Pat. No. 3,051,868) coupled with a quadrupole ion analyzer (Pat. No. 2,939,952) in a straight line arrangement. This straight line arrangement and the choice of components thereof minimizes complexity, costs, weight and bulk and on the whole provides good sensitivity and resolution. However, a significant component of noise in the form of light energy is picked up at the multiplier and the multiplier amplifies this photon noise along with the desired signal of ion current. It was discovered that by a specific structural modification of the cold cathode ion source the problem of low signal-to-noise ratio of the instrument could be attenuated.

OBJECTS OF THE INVENTION

It is the object of the present invention to provide an improvement in cold cathode ion sources and mass spectrometers utilizing such ion sources to enhance their utility for the above stated applications by improving the signal-to-noise ratio of the spectrometer consistent with retained high sensitivity and resolution, low weight and bulk, simplicity and economy of the instrument as a whole.

GENERAL DESCRIPTION OF THE INVENTION

The mass spectrometer of the invention utilizes an essentially straight line alignment of an ion source, nonmagnetic analyzer and electron-multiplier collector. Noise is reduced by a particular cold cathode ion source construction which mitigates against reception by the collector of photon noise generated in the ion source. This desirable feature of operations is obtained by the use of an axially extending cathode rod stub, hollowed at its free terminus and which rod, when viewed through the ion exit aperture of the source, presents a substantially photon-free view.

SPECIFIC DESCRIPTION OF THE INVENTION

The invention is now specifically described with reference to the accompanying drawings wherein FIGS. **1** and **2** are schematic sectional views of the apparatus of the invention, or critical portions thereof, showing two embodiments of the apparatus.

Referring now to FIG. **1**, there is shown a mass spectrometer **1** with a cylindrical body having an inlet opening **2** at one end surrounded by an inlet flange **3** (alternatively the flange opening could be in the side of the cylindrical body).

There are three major components of the spectrometer — a cold cathode ion source **10**, a quadrupole ion analyzer **20** and electron multiplier/ion collector **30**. Associated with the spectrometer is an output reading and/or recording means **40**.

The ion source **10** represents an important modification of the Blum and Torney ion source described in the authors' hereinbefore cited article. It comprises an open-ended cylindrical anode **11** with essentially plate form discharge cathodes **12** and **13** located at the respective ends thereof. Said discharge cathodes **12** and **13** may also comprise auxiliary cathodes or polished cathode margins **12A** and **13A** whose function and precise structure are more fully described in Pat. No. 3,051,868. Downstream cathode **13** bears a centrally located ion discharge exit aperture **14** through which ions are extracted into analyzer **20**. Upstream cathode **12** is provided with a cathode stub **15** located at the center thereof and extending at least partially into the space defined by cylindrical anode **11**. A critical feature of said cathode stub **15** resides in the provision of a hollowed-out free terminus **16** thereon, the function of which will be discussed in more detail hereinafter. This hollowed-out feature of the terminus **16** may be provided such as by employing a tubular construction of the entire stub cathode **15** (as shown in FIG. **1**) or, alternatively, as shown in FIG. **2** by employing a solid cathode stub **60** which is inwardly "dished" at the free terminus **65** thereof. A magnetic field produced by an externally or internally arranged magnet **19** threads the ion source structure as indicated by the arrow H.

The quadrupole analyzer **20** comprises four rods **21** and may also desirably comprise an entrance aperture **17** and an exit aperture **18**. The spacing of the quadrupole analyzer **20** from ion source **10** and electron multiplier/collector **30** is enlarged in the drawing for purposes of illustration.

The electron multiplier/collector **30** comprises an electron multiplier comprising an ion accelerating screen grid **31** and a plurality of dynodes **32**, and a collector **39**.

The secondary electron current at collector **39** is read out by bracketed means **40** which comprises a counting preamplifier **41**, pulse amplifier **42** and a scaler **43**. Alternatively, the read-out means can comprise an electrometer.

The use of an electron multiplier improves the sensitivity (and range) and signal-to-noise ratio of the instrument as a whole by amplifying the ion current output of the analyzer through several stages of secondary electron emission. However, the gain stability of commercial multipliers is ordinarily inadequate to provide reproducible data unless the gain is constantly reviewed or recalibrated. The latter step is ineffective in working at the lowest levels of ion current (corresponding to pressures of about 10^{-9} mm. Hg. to be measured) and is, in any case, tedious. This second order problem is solved by the use of counting technique read-out which is tolerant of variable gain and, when all ions are counted, is independent of mass and charge of collected ions. Additionally, the counting technique allows discrimination against a portion of the noise by means of pulse height analysis and allows a direct output for digital data acquisition. The only drawback of counting technique is the cost and complexity of the circuitry involved. However, on the whole, it is normally a desirable feature in the instrument.

In working with the combination described above but with a continuous rather than hollow terminused cathode stub **15**, major noise problems were discovered at high vacuum operating pressures. Specifically, a pressure and anodevoltage dependent noise was noticeable at these low pressures and research has shown that the noise is not attributable merely to leakage currents or the like. It was discovered that the cold cathode ion source was the source of this noise. It is surmised that the origin of such noise resides in the production of photons within the ion source and the emission therefrom of soft x-rays which, absent the hollow terminused cathode stub of the invention, are produced at a locus directly received by the collector. It was further surmised that the critical portion of the ion source with respect to this problem was the terminus of the cathode stub, since it comprised substantially the only internal ion source structure positioned in line of sight relationship with the collector. This surmise may or may not be correct. But in acting upon it, the cathode stub was modified to the hollow terminus style of the invention with excellent results in attenuating the noise problem, thereby vastly increasing the utility of the resulting overall instrument.

As mentioned, the key structural modification involved is the provision of hollow terminus **16** in cylindrical stub **15** as shown in FIG. **1**. Apparently, the collector **30** views the hollow interior of the stub terminus **16** which is field free and thus produces few if any photons. The stub **15** outer diameter is preferably equal to or slightly larger than the diameter of ion exit aperture **14**. Generally, the length of cathode stub **15** is about one-half the distance from its associated cathode **12** to the cathode **13**. The cathode stub is disposed along the central axis **50** of the device. The above dimensions and geometric relationship are desirable for optimum sensitivity and resolution of the ion current signal produced by the source. The reduction of photon noise is achieved by the hollow terminused stub configuration without disturbing these other optimum dimensions.

FIG. **2** shows a second embodiment of the invention in which the cathode stub **60** of an ion source **210** is of generally a solid construction and has an average outer diameter less than that of aperture **14**. However, terminus **65** is provided with the critical hollowed feature by dishing thereof. Additionally, flared edge **68** is of equal or preferably somewhat greater diameter than the diameter of aperture **14**. The cathodes **12**, **13** and the anode **11** are as in the FIG. **1** specie and the auxiliary cathodes or equivalents (such as polished edges of **12A** and **13A**) of FIG. **1** are not shown.

Testing has shown a substantial reduction of ion source derived photon noise through the use of the improved ion source of the present invention without loss of instrument sensitivity and resolution and without the addition of any significant weight, bulk, complexity or cost to the instrument.

In experiments with the ion source species of FIGS. **1** and **2** it was found that the employment of the tubular cathode stub of the FIG. **1** specie yielded a 50-fold reduction in photon noise compared with a mass spectrometer equipped with a cathode stub having a continuous terminus profile in the ion source. That is, the FIG. **1** specie had only one-fiftieth the noise of the prior Blum and Torney device. The FIG. **2** specie, comprising the solid stub cathode having the dished and outwardly flared terminus, effected a further reduction in noise by a factor of 3. Each of the **1** and **2** species appears to provide easy starting of the ion source at low pressures. Further, high sensitivity is maintained in both the FIGS. **1** and **2** species.

The cold cathode ion source of the present invention can be combined with other known techniques of spectrometer noise reduction (e.g., a slightly offset multiplier as shown in Bennewitz and Wedmeyer, 172 Zeitschrift fur Physik 1-18(1963)), although at a cost of some complexity, cost and loss of sensitivity by a factor of about two.

Still other variations within the scope of the present invention will be apparent to those skilled in the art. Accordingly, it is intended that the present disclosure shall be construed as illustrative in nature and not as limiting of the invention.

What is claimed is:

1. A cold cathode ion discharge source comprising a cylindrical anode having open ends and a central longitudinal axis; first and second plate form discharge cathodes located at the respective ends of said anode, each said plate form cathode being substantially perpendicular to said axis,

said second cathode having an ion exit aperture therethrough in coaxial alignment with said axis and in open communication with the space defined by said anode,

said first cathode comprising a stub extending into the space defined by the cylindrical anode and in coaxial alignment with the longitudinal axis thereof, said stub having its terminus located short of the ion exit aperture of said second cathode, said terminus being open-ended and hollowed out to a depth sufficient to prevent glow discharge therefrom.

2. The cold cathode ion source of claim 1 wherein the diameter of the terminus of said stub is equal to or greater than the diameter of said ion exit aperture.

3. The cold cathode ion source of claim 1 wherein said stub is of essentially solid construction and is dished inwardly at its terminus.

4. The cold cathode ion source of claim 1 wherein said stub is of tubular construction.

5. The cold cathode ion source of claim 1 wherein the terminus of said stub is flared.

6. The cold cathode ion source of claim 1 where the length of said stub is sufficient to locate the terminus thereof at about mid-way between said first and second cathodes.

7. A mass spectrometer comprising

A. a cold cathode ion discharge source comprising a cylindrical anode having open ends and a central longitudinal axis; first and second plate form discharge cathodes located at the respective ends of said anode, each said plate form cathode being substantially perpendicular to said axis,

said second cathode having an ion exit aperture therethrough in coaxial alignment with said axis and in open communication with the space defined by said anode,

said first cathode comprising a stub extending into the space defined by the cylindrical anode and in coaxial alignment with the longitudinal axis thereof, said stub having its terminus located short of the ion exit aperture of said second cathode, said terminus being open-ended and hollowed out to a depth sufficient to prevent glow discharge therefrom,

B. analyzer means located downstream from the ion exit aperture of (A) and in coaxial alignment with said longitudinal axis of said cylindrical anode, and

C. ion collector means located downstream from said analyzer means and having an ion collector entry in coaxial alignment with said longitudinal axis of said cylindrical anode.

8. The mass spectrometer of claim 7 wherein the analyzer means of (B) is of the quadrupole type.

9. The mass spectrometer of claim 7 wherein the terminus of said stub is flared.

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