

May 27, 1969

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3,446,964

METHOD OF SUPPRESSING PHOTOIONIZATION OF A GAS SAMPLE
IN AN ELECTRON CAPTURE DETECTOR

Filed Feb. 24, 1966

Sheet 1 of 2

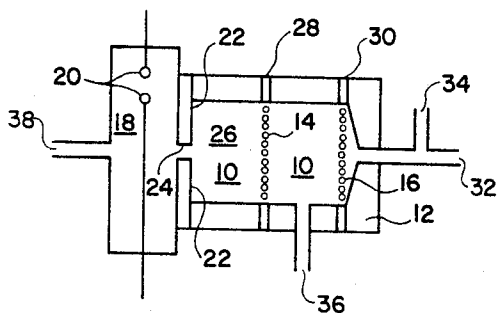


FIG. 1

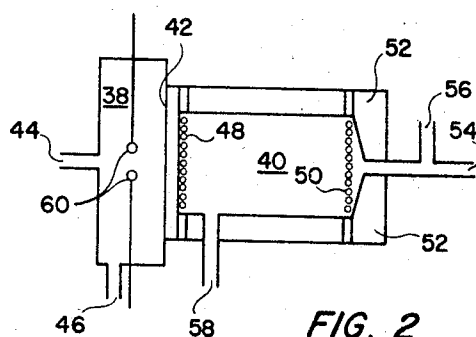


FIG. 2

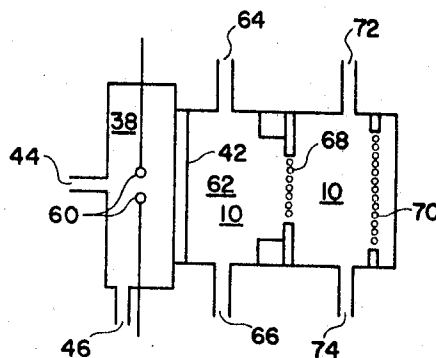


FIG. 3

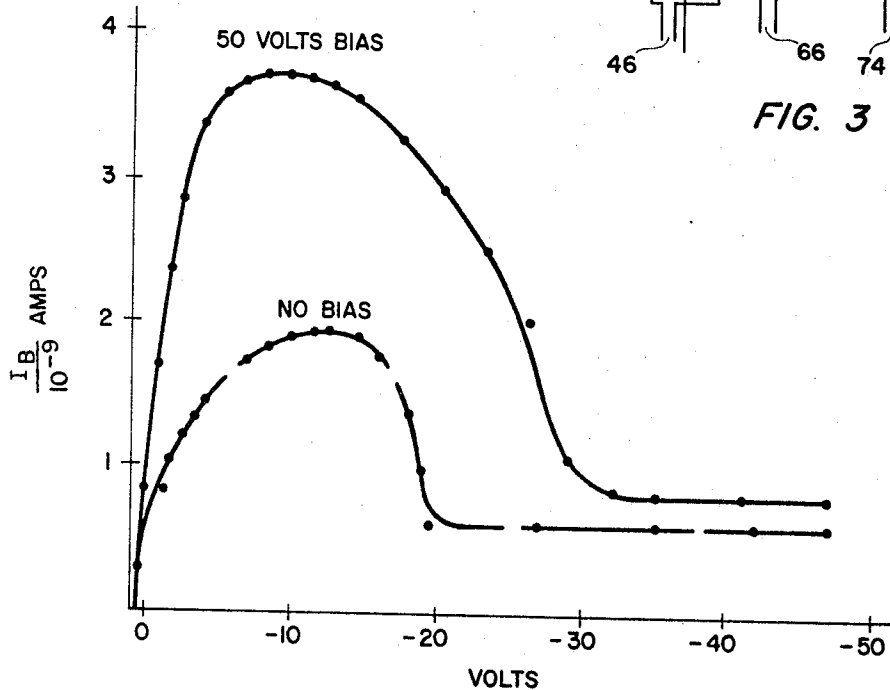


FIG. 4

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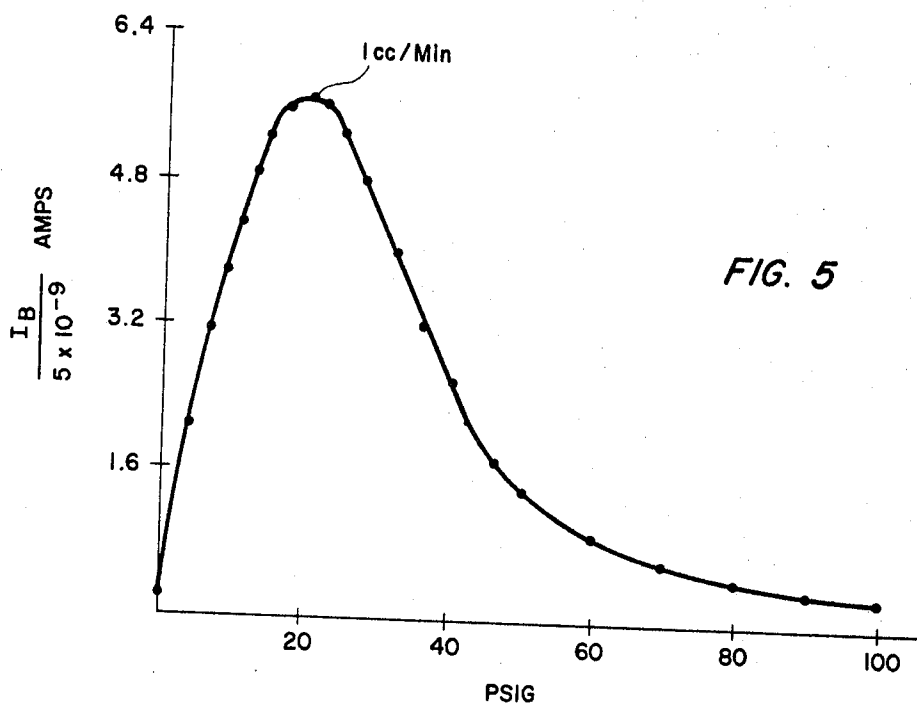
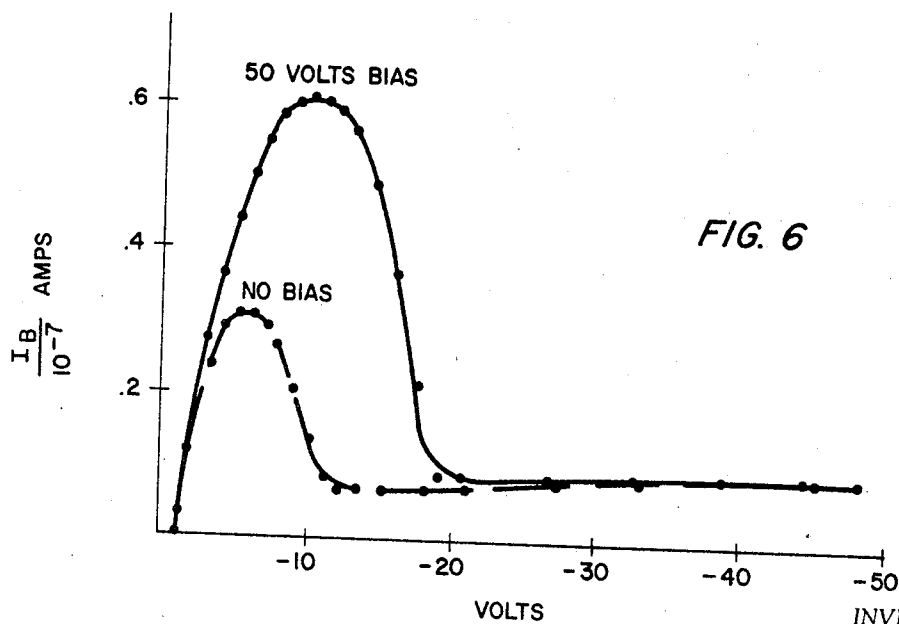
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Filed Feb. 24, 1966, Ser. No. 529,861
Int. Cl. G01t 1/18

U.S. Cl. 250—83.6

12 Claims

ABSTRACT OF THE DISCLOSURE

A method of operating an electron capture detector having a detection chamber including a polarizing electrode and a collector electrode and including a discharge chamber containing a source of excitation which also emits an ultraviolet light. The method includes the step of adding a photoabsorbing gas into the detection chamber for absorbing energy of the ultraviolet energy below the ionization potential of the sample gas to be detected thereby suppressing the ionization of the sample gas by the ultraviolet energy.

Disclosure

This invention relates to a method of operating, in the electron capture mode, a detector used for example, in gas chromatography and, more specifically, to such a method including the addition of a photoionizing gas to the detection chamber to establish the background current and suppress photoionization of sample.

An electron capture detector is described by Lovelock and Lipsky in an article entitled "Electron Affinity Spectroscopy" in the *Americal Chemical Society Journal*, volume 82, part 1, Jan. 20, 1960, pp. 431-33 and in co-pending application Ser. No. 359,827, Bochinski and Sternberg filed Aug. 15, 1964, now Patent No. 3,378,725, entitled "Electron Capture Detector" and assigned to the assignee of the present invention. Such detectors are widely used in the analysis of electronegative materials such as pesticides, steroids and amino acids and are particularly advantageous because of their great sensitivity and high degree of selectivity. Such a detector is available from the assignee hereof under the model No. 102650 Electron Capture Detector. In providing a source of electrons for such a detector, it has been found that far ultraviolet light is often generated at the same time when using an electrical discharge source; even when steps such as offsetting the discharge electrodes are taken to keep this light out of the detection chamber, a certain amount of it will penetrate the chamber with resulting photoionization of the sample and dilation of electron capture response. This photoionization effect yields a response in the opposite direction to that of the electron capture effect. Detectors employing the photionization principle where the photoionization of sample is the measured quantity such as those described in U.S. Patent No. 3,171,028, Lovelock and by Mikiya Yamane in an article entitled "Photoionization Detector for Gas Chromatography" in the *Journal of Chromatography*, volume 14 (1964) pp. 355-367, are known in the prior art.

It is the main purpose of the invention to provide a new and improved method of operating an electron capture detector by adding a photoabsorbing gas to the detection chamber to absorb far ultraviolet light, suppressing photoionization of sample and enhancing electron capture response.

An ancillary purpose of the invention is to add such a gas which will enhance electron mobility due to inelastic collisions of the electrons with the gas which will decrease their random motion and make them easier to collect increasing sensitivity due to increased probability of capture.

These and other objects are achieved by providing a method of operating an electron capture detector having a detection chamber including a polarizing electrode and a collector electrode, and a discharge chamber containing a source of excitation giving off far ultraviolet light, characterized by the steps of adding a photoabsorbing gas to the detection chamber which will absorb energy down to a point below the ionization potential of the sample gases to be detected, and adjusting the amount of photoabsorbing gas so that it absorbs substantially all of the ultraviolet energy entering the detection chamber from the discharge chamber capable of ionizing the sample.

Other features which are believed to be characteristic of the invention are set forth with particularity in the appended claims. The invention, and further objects and advantages thereof, can best be understood by reference to the following description and accompanying drawings in which—

FIG. 1 illustrates schematically one embodiment of a detector which may be used in carrying out the method of the invention wherein discharge gas flows from the discharge chamber into the detection chamber;

FIG. 2 shows a second embodiment of a detector for carrying out the method of the invention in which a gas-impervious, far ultraviolet transmitting window is positioned between the discharge and detection chambers;

FIG. 3 shows another embodiment of a detector capable of carrying out the method of the invention containing the window, as in FIG. 2, and provided with separate means for passing the photoabsorbing gas primarily through an intermediate zone of the detection chamber and the carrier and sample gas primarily between the polarizing and collector electrodes;

FIG. 4 is a graph of background current versus polarizing voltage with helium carrier for a detector, such as illustrated in FIG. 1;

FIG. 5 is a graph of background current versus carbon dioxide p.s.i.g. for an embodiment such as illustrated in FIG. 1; and

FIG. 6 is a graph of background current versus polarizing voltage with both helium carrier and carbon dioxide again in an embodiment such as illustrated in FIG. 1.

Turning now to the drawings, in FIG. 1 there is illustrated a detector having a detection chamber 10 which is contained in a housing 12, and has a polarizing wire grid electrode 14, and a collector wire grid electrode 16, both of which may be platinum. The detector also has a discharge chamber 18, containing a pair of discharge electrodes 20. A plate 22, having a small central aperture 24, is positioned between the discharge chamber 18 and the detection chamber 10, forming an intermediate zone 26 in the chamber 10, which is located between the plate 22 and the polarizing electrode 14. The polarizing electrode 14 and the collector electrode 16 are provided with terminals 28 and 30, respectively, for making an electrical connection thereto. Detection chamber 10 is provided with an inlet port 32 through which carrier gas and sample may be injected and a second inlet port 34, downstream of port 32, through which a photoabsorbing gas may be injected. Chamber 10 is also provided with a vent port 36. Discharge chamber 18 is provided with an inlet port 38 through which the discharge carrier gas is injected. The discharge supporting gas then flows through the hole 24 and out vent 36. A deflector

plate, not illustrated, may be used to provide a more uniform sweeping of gas through discharge chamber 18.

In operating a detector of the type illustrated in FIG. 1, the discharge electrodes 20 may be placed off-center, out of line with the port 38, the hole 24 and the port 32, for the purpose of minimizing the amount of ultraviolet light which would get into the detection chamber 10, and particularly that portion thereof between electrodes 14 and 16, in order to avoid photoionization of the sample gas. This has not, however, been found to be completely effective and gave rise to the discovery of the method of the present invention, which adds a photoabsorbing gas into the detection chamber 10 which will absorb the far ultraviolet energy and suppress photoionization of the sample gases which are to be detected. Examples of photoabsorbing gases which may be used are CO₂, N₂ and propylene, or any other gas which does not capture electrons and which will absorb far ultraviolet light of wavelengths shorter than that corresponding to the ionization potential of the sample to be detected and of impurities which may be present.

There is a possibility of contaminating the discharge electrodes 20, particularly when a gas such as the latter of these gases is used and diffuses into the discharge chamber 18. This may be avoided by using an embodiment such as illustrated in FIG. 2, in which the discharge chamber 38 is separated from the detection chamber 40 by means of a gas-impervious, far ultraviolet transmitting window 42 which may be of lithium fluoride, calcium fluoride or magnesium fluoride, for example. In this embodiment the discharge carrier gas enters through the inlet port 44 and leaves through the vent port 46. The polarizing electrode 48 may be placed adjacent the window 42, if desired. The collector electrode 50 is in the other end of the housing 52 which contains the detection chamber 40. Carrier gas and sample enters the detection chamber 40 through the inlet port 54. Photoabsorbing gas may enter the chamber 40 through the inlet port 56. Both of these gases exit through vent port 58. In this embodiment, the discharge electrodes 60 are shown as centered. With the use of the method of the present invention, it is also possible to center the discharge electrodes 20 of FIG. 1, since the far ultraviolet light is absorbed by the photoabsorbing gas and photoionization of sample is substantially suppressed. Also, with the addition of the photoabsorbing gas in sufficient quantity, it is possible to move the polarizing electrode 14 of FIG. 1 back toward the plate 22. It is also obvious, from the embodiment of FIG. 2, that the discharge chamber 38, discharge electrodes 60 and the discharge carrier gas may be completely replaced by an ultraviolet lamp having a suitable far ultraviolet transmitting window.

A still further embodiment of a detector which may be employed in carrying out the objects of this invention is illustrated in FIG. 3. This embodiment has a discharge chamber 38, similar to that of FIG. 2, with discharge electrodes 60, inlet port 44, vent port 46 and window 42. An intermediate zone 62 is provided in detection chamber 10, having an inlet port 64 and a vent port 66, between window 42 and polarizing electrode 68, through which the photoabsorbing gas may flow. The detection chamber 10 also includes a second portion between the polarizing electrode 68 and the collector electrode 70, including an inlet port 72 and a vent port 74 through which carrier gas and sample are caused to flow. Again, obviously the discharge chamber 38 and associated components may be replaced by an ultraviolet lamp.

Turning now to a discussion of the operation of the embodiment shown in FIGS. 1-3 in accordance with the method of the invention, first, the embodiment shown in FIG. 1 will be discussed when operating using CO₂ as the photoabsorbing gas. First, the discharge carrier flow rate into port 38 is set high enough, for example 120 cc./min. for 1/8 inch packed columns, at least twice but preferably three to five times the volume flow rate of

the sample carrier, in order to limit back-diffusion into the discharge chamber 18. This may be helium. Gases such as nitrogen, oxygen, air, hydrogen, nitrous oxide, or carbon dioxide may also be added to the discharge carrier in order to stabilize the discharge and lower the energy thereof. Second, the sample carrier flow rate through port 32 is set. Typical sample carrier gases are helium and nitrogen. Next, after setting the discharge voltage across the electrodes 20 to provide a fixed current, the voltage on the polarizing electrode 14 is set to give peak background current at collector electrode 16.

The voltage applied to the polarizing electrode 14 is the most important single factor controlling the detector characteristics, since electrode 14 both regulates the flow of electrons from the intermediate zone 26 to electrode 16, and determines the collection efficiency of those electrons which go through it. The effect of the polarizing electrode 14 is seen in the curve of FIG. 4 which shows data taken on a detector of the type illustrated in FIG. 1. The peak current is obtained at a potential corresponding to the space charge potential found at the electrode 14 when it is floating. As the polarizing voltage is made less negative, electrons from the intermediate zone 26 are increasingly collected at the electrode 14, and those electrons passing through electrode 14 are less efficiently collected, resulting in decreasing detector current. As the polarizing electrode voltage is made more negative than its space charge value, electrons from the intermediate zone 26 are repelled, although those still getting through electrode 14 are more efficiently collected at electrode 16. At a sufficiently high negative polarizing electrode voltage, the supply of electrons from the intermediate zone 26 is completely blocked and the much lower current observed results solely from photoionization of column bleed and other impurities brought into the detector.

The lower of the two curves in FIG. 4 illustrates an embodiment where the discharge anode of discharge electrodes 20 is at ground potential (no bias). When the discharge is biased at a more negative potential by placing the discharge anode 20 at minus 50 volts instead of ground potential, as illustrated in the upper curve of FIG. 4, more discharge electrons enter the intermediate zone 26 and the detector current is increased at lower voltages. The detection chamber photoionization current obtained at high negative polarizing voltages remains unchanged by biasing voltage.

The next step is to add CO₂ through port 34 to give maximum background current. The effect of carbon dioxide on background current is shown in FIG. 5, again a curve taken on a detector of the type illustrated in FIG. 1. Addition of carbon dioxide increases the background current until a maximum is reached which, in this case, was about 1 cc./min. of carbon dioxide. Further addition of this gas then decreases the background current. The observed behaviour can be explained on the basis of photoionization of carbon dioxide by the far ultraviolet light from the discharge increasing the electron concentration in the detection chamber, and particularly in the intermediate zone 26. This leads to an increasing current in the detection chamber 10 until the positive ion space charge effectively reduces the electron collecting field sufficiently to decrease the observed current. The higher the polarizing voltage, the higher the flow rate of carbon dioxide required for maximum current. Other data shows that optimum sensitivity and discrimination are obtained at or near the carbon dioxide flow giving the maximum background current.

After adding the CO₂ to give the maximum background current, the polarizing voltage on polarizing electrode 14 may be reset to give a selected fraction of peak background current which may be low for weak capturers and higher for strong capturers. After this step, the rate of introduction of carbon dioxide is reset to maximize the background current again. Also, if it is desired to further suppress photoionization in measuring samples of lower ionization potential, or in measuring

capturing samples in the presence of photoionizing contaminants, which might be other constituents in the sample, the rate of introduction of CO₂ may be further increased.

The addition of CO₂ also serves to increase the mobility of the electrons, permitting them to be more readily collected due to inelastic collisions with the CO₂ molecules which serve to slow them down, decreasing their random motion and with less resulting backward motion in the field and increasing the probability of collection. The electrons thermalized by collision with CO₂ molecules are also more readily captured by electron capturing species.

Current-voltage curves obtained from a detector of the type illustrated in FIG. 1 with added carbon dioxide are shown in FIG. 6. They indicate the same general characteristics as those obtained with helium alone, shown in FIG. 4. Both positive ion space charge in the zone 26 and the higher electron mobility with carbon dioxide contribute to the shift of the maximum of the curve to a lower polarizing voltage. The effect of bias voltage is similar to that found with helium alone, including the independence of the detection chamber photoionization current on bias voltage.

Responses of the detector to capturing and non-capturing substances are shown in the table below where the capturing sample consisted of 20 picograms of lindane and the non-capturing sample consisted of 15.5 micrograms of hexadecane. The ratio of non-capturer to capturer required to elicit an equivalent amount of response is also shown and is labeled "Discrimination Factor."

A comparison of responses shown for helium carrier without and with addition of small amounts of nitrogen and carbon dioxide to the column effluent demonstrates the improved response and discrimination obtainable through the use of added gases, which particularly improve discrimination by absorbing far ultraviolet photons which can photoionize hexadecane. The far ultraviolet absorption also contributes to the improved lindane response by shielding the lindane from possible photoionization, which would diminish its capture response, and by providing additional electrons through photoionization of the added gas. The added gases also enhance the electron mobility and lower the average electron energy from the levels found in helium alone.

TABLE.—RESPONSE AND DISCRIMINATION IN PERCENT OF BACKGROUND

	Lindane (20 picograms)	Hexadecane (15.5 micrograms)	Discrimination factor
He.....	3	135	.017×10 ⁶
He+CO ₂ ...	5	3	1.3×10 ⁶
He+N ₂	3	4	0.58×10 ⁶

With embodiments such as illustrated in FIGS. 2 and 3, employing the far ultraviolet window 42 which, as suggested, may be lithium fluoride, the energy range of the photons penetrating window 42 normally would not affect the sample, but would only ionize the photoabsorbing gas. Under these conditions, CO₂ may be used but a better gas is propylene. As stated above, propylene is not normally used in a configuration such as FIG. 1 because of the tendency of the gas to contaminate the electrodes 20 due to back-diffusion through the hole 24. In the embodiments of FIGS. 2 and 3, when using a lithium fluoride window, the photoabsorbing gas may have an ionization potential of less than 11.8 electron volts, equivalent to the energy range passed by the window, or preferably less than 10 electron volts, which is slightly higher than the 9.8 electron volt ionization potential of propylene. In these embodiments the ionization of the photoabsorbing gas is the sole source of electrons and the background current is set by merely increasing the flow of propylene or other photoabsorbing gas until the background current peaks at the collector electrodes 50 or 70, for any fixed rate of introduction of ultraviolet light into the detection chambers 40 or intermediate

zone 62 caused by a fixed discharge at electrodes 60. In the embodiment illustrated in FIG. 3, the photoabsorbing gas such as propylene is introduced through the port 64 and primarily exits through the port 66, whereas the sample gas is introduced through the port 72 with its carrier and primarily exits through the port 74. This places the photoabsorbing gas generally closer to the source of ultraviolet light, again tending to further suppress the photoionization of the sample.

In an embodiment such as illustrated in FIG. 1, even with the discharge electrodes 20 off-center, as illustrated, it was estimated that out of the total electrons entering the portion of the chamber 10 between electrodes 14 and 16, only approximately one-fourth of them were due to direct boil-off from the discharge and that photoionization of the photoabsorbing gas CO₂ in the intermediate zone 26 accounted for approximately three-quarters. Where previous detectors, such as those disclosed in the Lovelock patent and by Mikiya Yamane in the article referred to above, have used a grid or an ion trap, respectively, to prevent ions or electrons from entering the detector chamber portion between the polarizing and collection electrodes, the subject invention attains exactly the opposite effect keeping the ionizing far ultraviolet energy from ionizing the sample in order to maximize the detector response due to electron capture by the samples.

Since the principles of the invention have now been made clear, modifications which are particularly adapted for specific situations without departing from those principles will be apparent to those skilled in the art. The appended claims are intended to cover such modifications as well as the subject matter described and to only be limited by the true spirit of the invention.

What is claimed is:

1. A method of operating an electron capture detector having a detection chamber including a polarizing electrode and a collector electrode, and a discharge chamber containing a source of excitation giving off ultraviolet light, comprising the steps of:

adding a photoabsorbing gas into the detection chamber which gas will absorb energy down to a point below the ionization potential of the sample gases to be detected and,

adjusting the amount of photoabsorbing gas so that it absorbs substantially all of the ultraviolet energy entering the detection chamber from the discharge chamber capable of ionizing the sample.

2. The method of claim 1 in which the photoabsorbing gas is CO₂.

3. The method of claim 2, including the steps prior to adding CO₂, of:

setting the discharge carrier flow rate through the discharge chamber into the detection chamber at a high enough flow rate to limit back-diffusion from the detection chamber into the discharge chamber; setting the carrier flow rate into the detection chamber; setting the voltage on the polarizing electrode to give approximately peak background current at the collector electrode;

and in which the step of adjusting the amount of photoabsorbing gas comprises:

increasing the flow of CO₂ until substantially maximum background current is achieved at the collector electrode.

4. The method of claim 3 including the added steps of:

resetting the polarizing voltage to give a selected fraction of peak background current, low for weak capturing samples or high for strong capturing samples; and,

resetting the CO₂ flow to again maximize collector background current.

5. The method of claim 3 including the step of:

further increasing the flow of CO₂ to further suppress photoionization of sample for samples of low ioniza-

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tion potential or when measuring in the presence of photoionizing contaminants.

6. The method of claim 1 in which the photoabsorbing gas is itself photoionizable and on absorbing the ultraviolet light from the discharge chamber provides a source of electrons for measurement of the sample by electron capture.

7. The method of claim 6 in which the photoabsorbing gas has an ionization potential of less than 11.8 electron volts.

8. The method of claim 6 in which the photoabsorbing gas has an ionization potential of less than 10 electron volts.

9. The method of claim 8 in which the photoabsorbing gas is propylene.

10. The method of claim 9 in which the step of adjusting the amount of photoabsorbing gas comprises increasing the propylene flow until background current peaks at the collector electrode.

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11. The method of claim 10 including the steps of: flowing the propylene primarily between the source of ultraviolet light and the polarizing electrode; and, flowing sample and carrier primarily between the collector and polarizing electrodes.

12. The method of claim 6 in which the discharge electrons are blocked from reaching the photoabsorbing gas while the ultraviolet light is passed into the detection chamber.

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U.S. Cl. X.R.

20 250—43.5; 315—111