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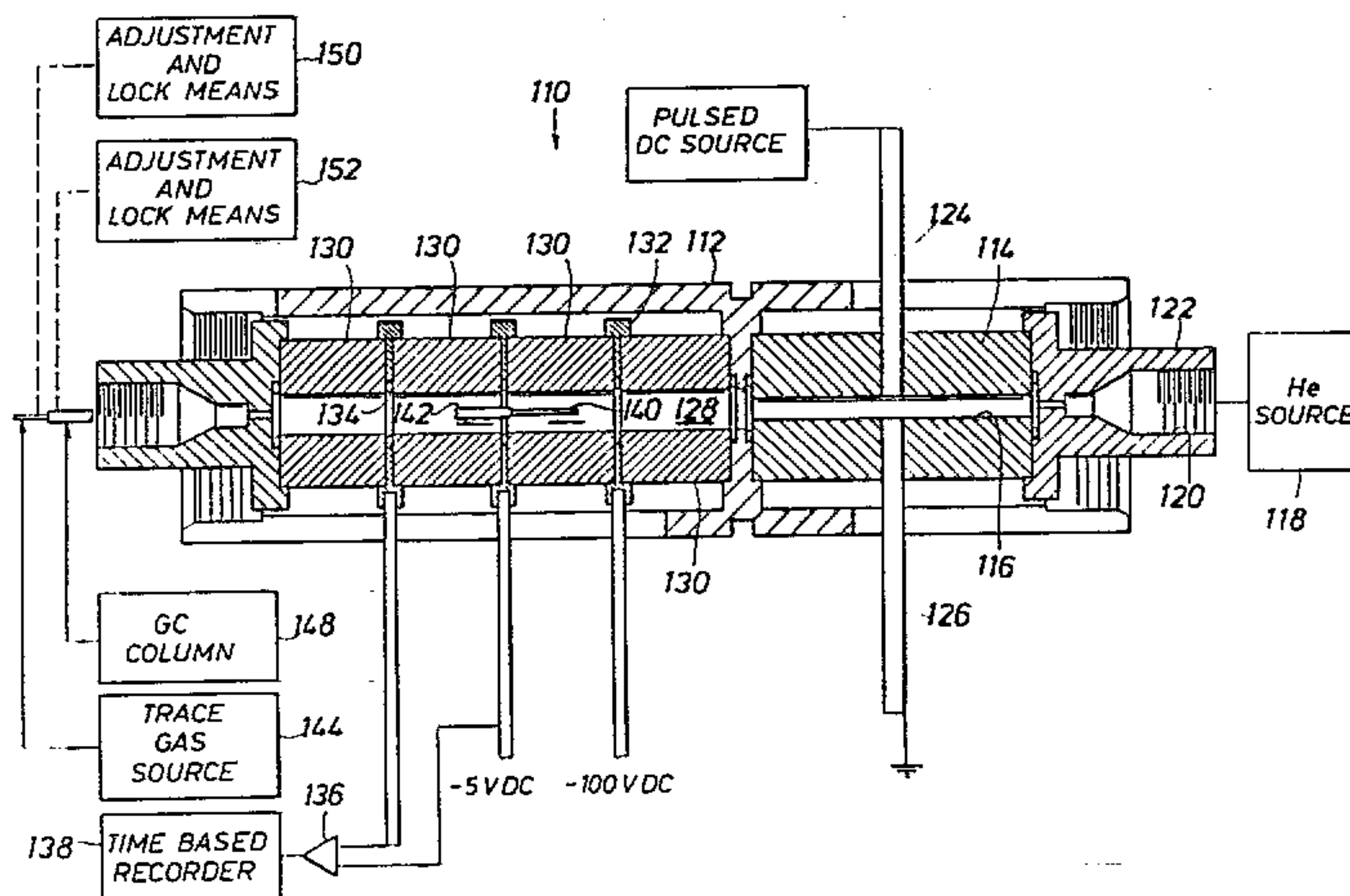
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(57) Abstract

The discharge systems of this disclosure are useful in the chemical analysis field, including identification and quantification of gaseous impurities. The systems utilize a pair of electrodes which apply a spark across a gap between the electrodes, the spark preferably being repetitively formed. As an inert gas flows between the electrodes, the spark creates photons of energy which are emitted and are used as described. In alternate aspects, other particles are energized in the spark gap and subsequently surrender their energy. Photon emission or loss of energy assists in identification and measurement of peaks eluted from a typical gas chromatograph. The preferred inert gas is helium with or without traces of rare inert gases.

IMPROVED PULSED DISCHARGE SYSTEMS

FIELD OF THE INVENTION

The invention generally relates to the art of gas analysis and more particularly to the analysis of gas through chromatographic means.

BACKGROUND OF THE DISCLOSURE

The discharge systems of this disclosure utilize a pair of electrodes which, in the preferred embodiment, apply a transverse spark across a gap between the electrodes, the spark preferably being repetitively formed. Bipolar or monopolar discharge can be used. An inert gas flows between the spark electrodes. The spark creates photons of energy which are emitted and are used as described. In alternate aspects, particles are cleared or energized in the spark gap and energized particles subsequently surrender energy. The preferred inert gas is helium with traces of inert gases. The photon emission or loss of energy assists in identification and measurement of gas chromatographic column (GC hereinafter) eluted peaks from a typical GC source.

SUMMARY OF THE INVENTION

Another aspect of the invention pertains to a method of analyzing a sample compound comprising the steps of flowing a carrier gas through a chamber for exposure to DC current thereby energizing at least one component of the carrier gas to an excited state as a result of exposure to the DC current, commingling a gaseous sample with the carrier gas within a chamber wherein the carrier gas comprises at least one component in an excited state, forming one or more excited compounds in the gaseous sample resulting from photon emission in the decay of at least one excited component of the carrier gas wherein the emissions involve an energy exchange up to about 11.8 eV and determining the type and concentration of one or more compounds in the gaseous sample by measuring photon emission from the decay of the excited compounds in the gaseous sample.

Further the invention comprehends a gas detector for identification and quantification of sample compounds, comprising an elongated chamber having a first chamber inlet at one end and an outlet at the other end and a gas flow path between the first inlet and outlet ends with two electrodes spaced apart and located to produce short, repeated, high voltage, pulsed DC current within the chamber across the gas flow path and wherein spark duration minimizes electrode erosion and permits observation of phenomena occurring at and between the

DC current at and remote from the electrode location. Means are provided for introducing a carrier gas into the chamber through the first chamber inlet and flowing the carrier gas in the gas flow path. Means are provided for introducing a sample gas into the chamber through a second inlet which is located downstream from the first chamber inlet and downstream from the two spaced electrodes and flowing the sample gas in the gas flow path whereby ions are produced by the spark or by metastable species of the carrier gas.

Still further the invention comprehends a method of testing an airborne sample comprising the steps of providing an airborne sample flowing through a test chamber, simultaneously providing a carrier gas flowing through the test chamber, within the test chamber, forming with an electrical current a metastable species in the carrier gas wherein the metastable species is characterized by having a ground energy state and excited state of sufficient time duration to enable an energy transfer from the excited state of the metastable species to the airborne sample by the emission of photons and wherein the excited state causes an energy transfer to the airborne sample wherein the excitation energy range of the metastable species is selected to preclude energizing the constituents of air.

Further still, the invention comprehends a method of analyzing an eluted sample compound in a carrier gas comprising the steps of flowing the carrier gas through a chamber for exposure to a spark discharge across the chamber, the spark discharge being formed across a pair of spark forming electrodes cooperating with a pulsed DC current source and introducing an eluted sample into the carrier gas downstream from the spark discharge and observing downstream in the chamber spark caused current flow in the chamber to analyze the concentration of the eluted sample compound flowing through the chamber by detecting changes in the current flow.

Still further the invention pertains to a charged particle detector comprising a closed chamber having a helium gas flow inlet at a first end and spaced outlet at a second end to enable helium flow therethrough and spaced electrodes cooperating with a pulsed DC power supply responsive to DC current flow sufficient to enable an electrical spark to be formed between the electrodes, the electrodes being positioned to form a spark in the helium flow into the chamber to thereby create photon emission. Spaced detector means are downstream in the chamber for collection of charged particles downstream of the spark across the gap wherein the

charged particles enable a current to be formed indicative of sample gas concentration in the chamber, an inlet downstream in the chamber controllably introduces a sample and carrier gas flow from a GC column at a selected location downstream from the spark forming electrodes so that the sample and carrier gas and the helium flow provide current for the detector means.

5 Means are provided for optimizing the current by adjusting the selected location for sample gas and carrier gas introduction and by adjusting voltage applied to the detector means.

Moreover the invention also comprehends a method for analyzing a sample compound comprising the steps of flowing a carrier gas through a chamber wherein the carrier gas comprises an inert gas and a dopant gas wherein the dopant gas is selected such that the
10 resonance energy of the dopant component is greater than the ionization potential of the compound to be measured in the gaseous sample, commingling a gaseous sample with the carrier gas within a chamber forming a composite gas, exposing the carrier gas to a spark generated by DC current and optically observing spark caused emissions in the chamber to analyze the gaseous sample component, wherein the emissions involve an energy exchange up to the resonance energy
15 of the dopant.

The invention also pertains to a charged particle detector comprising a circular closed chamber having a gas flow inlet and spaced outlet positioned to direct gas flow through the chamber and the chamber directs the gas flow in a circle therein with spaced electrodes provided with a current sufficient to enable an electrical spark to be formed in a gap between the
20 electrodes locating the spark thereacross, the electrodes being positioned to form a spark in gas in the chamber to create charged particles. A spaced detector electrode is in the chamber for collection of charged particles wherein the charged particles move to the detector electrode to form a current indicative of a sample gas concentration in the chamber.

Moreover the invention in another aspect pertains to a gas detector for
25 identification and quantification of sample compounds, comprising a circular chamber having a tangential chamber inlet and a tangential outlet and a circular gas flow path between the inlet and outlet ends, means for flowing an inert gas into the chamber and two spaced electrodes located in the chamber to produce repeated current sparks across the chamber wherein gas interaction forms energized particles in the chamber. A sample source is connected to deliver gas into the
30 chamber and means is responsive to interacted sample gas and charged particles to enable sample

gas detection in the chamber.

Yet further the invention comprehends an electron capture detector comprising a closed chamber having a helium flow inlet to enable helium flow therethrough, spaced electrodes forming a spark between the electrodes defining a spark thereacross, the electrodes being positioned in the chamber to form a spark through helium in the chamber. A sample gas source is connected to an inlet to the chamber to provide sample gas flowing in the chamber and the chamber and the inlet are constructed and arranged to flow gas in a circle in the chamber. A spaced detector in the chamber is provided for collection of current formed as a result of the spark across the gap wherein the spark irradiated helium enables a current to be formed indicative of eluted gas sample concentration in the chamber and the detector measures the gas sample in the chamber by change in current flow.

Another aspect of the invention comprehends a method for analyzing a sample gas comprising the steps of exposing a first gas in a closed spark chamber to DC current across the chamber, energizing at least one component of the first gas to an excited state as a result of exposure to the DC current and permitting the excited gas to form ionizing radiation by decay, exposing a sample gas in a sample chamber to ionizing radiation resulting from the decay of at least one component of the first gas, forming charged particles in the sample chamber as a result of exposure to the ionizing radiation, measuring the charged particles wherein the measurement occurs in timed relationship to charged particle formation and selectively determining concentrations of compounds contained in the sample gas by utilizing the measurements.

Still another aspect of the invention provides a method for selectively analyzing a sample of air for impurities comprising the steps of exposing a source gas comprising krypton in a closed spark chamber to DC current, energizing the krypton to an excited metastable state as a result of exposure to the current, exposing the sample of air to ionizing radiation formed by the decay of the metastable krypton within the closed spark chamber where the ionizing radiation passes from the closed spark chamber into an adjacent sample chamber through a membrane window, forming charged particles within the sample chamber by the selective ionization of impurities within the air sample while precluding the ionization of major constituents of air and determining concentrations of the impurities based upon measured magnitudes of the charged particles.

DESCRIPTION OF THE DRAWINGS

Fig. 1 is a sectional view through a spark operated system utilizing helium to test GC column peaks wherein an output signal is formed by ring shaped electrodes.

Fig. 2 is an alternate embodiment incorporating three ring shaped electrodes with a bias voltage and further including a trace gas input.

Fig. 3 is an alternate structure utilizing a sample input downstream of facing electrodes and utilizing a set of spaced rings connected with selected voltages.

Fig. 4 is a timing chart showing the timing sequence of coil charging circuitry for pulse formation.

Fig. 5 is an alternate embodiment in which helium is mixed with rare inert gases.

Fig. 6 graphs emission radiation and ionization potential.

Fig. 7 shows several detector chambers provided with rare gases for analysis.

FIG. 8 is an alternate system showing dopant added to the helium.

Figs. 9A and 9B graph certain ratio measurements to determine sample identification.

Fig. 10 is an alternate embodiment showing a round chamber utilizing circular flow.

Fig. 11 is an exploded view of the round chamber in Fig. 10 and electrodes in the chamber.

Fig. 12 is a side view of the round chamber.

Fig. 13 shows in air analyzer.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In Fig. 1, a detector 10 uses helium from a helium source 12 regulated above atmospheric pressure flowing from right to left. A GC column 14 provides flow of solvent and eluted sample. GC column 14 connects to a sample injection tube 16 moved and clamped by an adjustment mechanism 18 to a desired location. The power supply 20 provides current for pulse forming circuit 22. Inverter 24 forms alternating positive and negative pulses. Conductors 26 and 28 are input to a differential amplifier 30 connected to time based recorder 32.

The detector 10 has an elongate cylindrical shell 34 around an elongate cylindrical sleeve 36 about passage 38. The passage 38 is between electrodes 40 and 42.

The housing 34 supports fitting 44 connected with the helium source 12. Ring 48

seals the body 36. Transverse web member 50 has a central opening 52 aligned at cylindrical spacers 54, 56 and 58. Circular electrode 60 forms a full circle around passage 64. At the surface of the passage 64, an exposed metal ring 66 connects to the circular electrode 60. A second circular electrode 62 is wider than the electrode 66. Sample tube 16 is axially moved to the left or right to vary current at electrometer 30. The sample tube 16 is inserted through the threaded detail 68 in the end fitting 70. The tube clamp and adjustment device 18 moves the sample tube 16 in and out to vary sensitivity and performance. The terminals 62 and 66 have an adjustable bias. Photon emission spectra through the passage 38 and 64 interact and charged particles are either formed or neutralized depending on the sample material creating current flow at electrodes 62 and 66.

Helium (slightly above atmospheric pressure) flows at about 20 - 120 milliliters per minute or between ten to thirty times larger than the flow from the tube 16. An elevated temperature may keep samples in the volatile state. Spark duty cycle is in Fig. 4. At 1000 pulses per second, a pulse is 10 microseconds or less.

FIGURE 2

An electron capture device (ECD) 110 has an elongate cylindrical housing 112 around cylindrical member 114 defining passage 116. Helium source 118 connects to a fitting detail 120 in a fitting 122. Spaced electrodes 124 and 126 terminate in parallel end faces on metal rods having a diameter of about 1/16" spaced approximately 1/16" across the passage 116. Smaller diameter of about 0.3 mm can be used. Larger electrodes having sharpened points transverse to the gas flow are permissible.

The passage 128 is defined by a spacer ring 130. Four similar rings are separated by three rings 132 with an exposed electrode ring 134. Rings 134 are first, second and third electrodes for operation of the ECD. The first ring has a negative 50 to 250 VDC and -100 VDC is optimum. The next ring bias is about -5 VDC. The third ring is permitted to float. The last two rings input to an electrometer 136 to measure current output to a time based recorder 138.

First and second injection tubes are concentric and move axially. Smaller tube 140 introduces a fixed flow of a trace gas 144. The second concentric tube 142 connects to the GC column 148. The tubes 140 and 142 are moved in ECD 110 and lock means 150, 152 lock the tubes at specified locations. Arrows indicate tube movement. Dopant gas and GC gas effluent are swept by the larger helium flow to the left past the electrometer electrodes to form a signal.

FIGURE 3

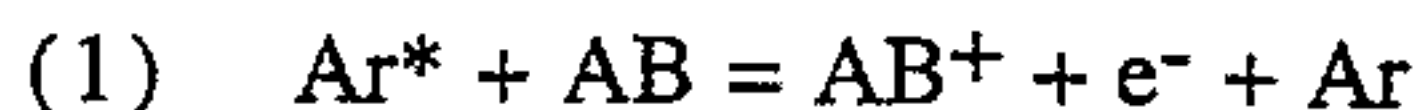
5 A detector system 220 utilizes a carrier gas source 212 to provide helium and about 0.3% argon. The carrier gas inlet opening 218 connects with right end cap 222 opposite the left end cap 223. The end caps plug the tube 221.

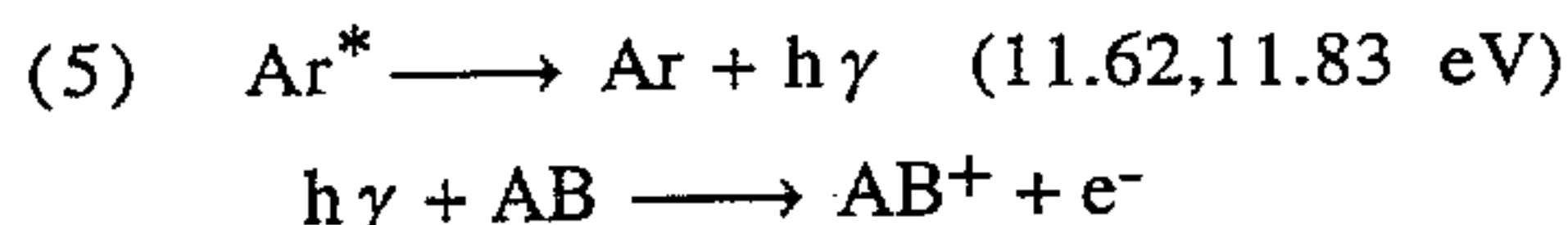
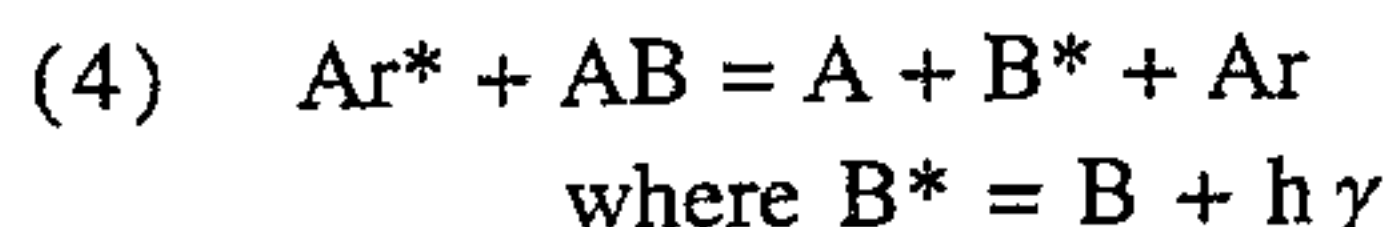
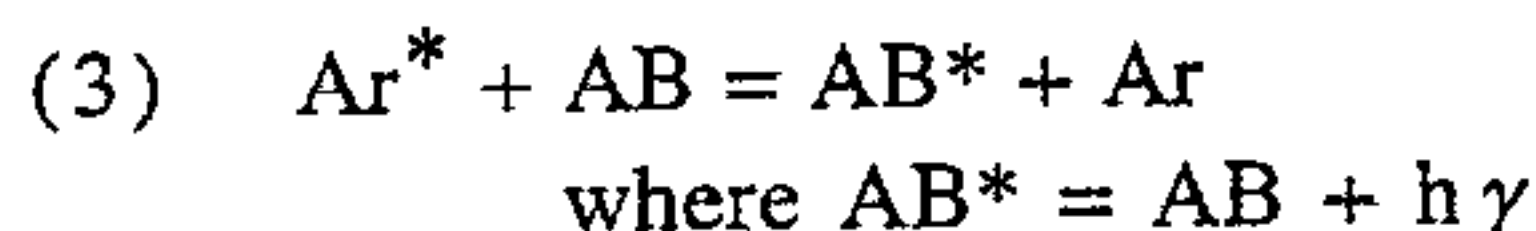
10 Spark gap 230 is between opposing, parallel faces on two electrodes 231 and 232 provided with a high voltage pulse. Sample gas from a source 229 is injected into the tube 221 at a port 235 from a GC column or the like. Exposed metal rings 226 are spaced along the tube 221 arranged serially downstream. Intermediate rings 226 are tied to series resistors 233 for voltage drops. Ring 227 is connected to an electrometer 228.

15 Electrodes 226 are connected to series resistors 233. B⁺ supply 234 voltage (positive or negative) attracts the desired charged particles. B⁺ voltage is pulsed and is controlled by a timer 216 and proportioned by resistors 233. The port 236 is aligned with the port 218 which also is an observation port during the spark. Photons impinge on an external spectrum analyzer 240
20 output to a recorder 241. Charging circuit 242 connects with a high voltage discharge circuit 243 to provide a timed pulse for firing.

25 In FIG. 4, the top curve shows the charging pulse 244 for high voltage discharge circuit 243. That circuit forms an output 248, a pulse of short duration. Detection is delayed by a specified time 252, and then a detection enable pulse 250 is formed.

30 Helium with a trace of argon flows into the spark gap 230 where ions and atoms are excited. Argon resonance lines are at 104.8 and 106.6 nm with corresponding energies of 11.62 and 11.83 eV. Excited argon (Ar*) from the spark gap 230 and sample compound AB from the port 235 are mixed. Possible ionization reactions are:





10 where e^- denotes a free electron, * denotes an excited state, and $h\gamma$ denotes spectral emission. Equation (3) and (4) reactions form characteristic emission spectra signals for identification and quantification. Equation (1) and (2) reactions produce free electrons measured with electrometer 228, with the measured current
15 increasing with increasing concentration of compound AB.

Ar* radiation at 11.62 and 11.83 eV will not ionize any compound with an ionization potential above 11.83 eV. Major components of air are nitrogen (15.6 eV), oxygen, (12.08 eV), water (12.6 eV), and carbon dioxide (13.8 eV). Air is not ionized and
20 impurities (pollutants) with ionization potentials below 11.83 eV are ionized.

FIGURE 5

25 In monitoring for unwanted pollutants (BF_3) in a plant making NO_2 , it is not possible to selectively ionize impurity BF_3 without ionizing NO_2 . An atmospheric sample of air (nitrogen, oxygen, water and carbon dioxide) may mask testing by emissions from air constituents. Selective ionization of helium with less than
30 1.0% trace rare gas creates a relatively slow diffusing flux of metastable helium which excites the dopant rare gases argon (Ar), krypton (Kr), xenon (Xe), or neon (Ne). The helium-argon gas emission has resonance lines at 104.8 and 106.6 nm. Argon emission therefore avoids ionizing air while ionizing impurities with ionization
35 potentials less than 11.8 eV. A helium-xenon gas has a resonance

energy of 9.57 eV which selectively ionizes compounds with lower ionization potential. Likewise, helium-krypton will produce resonance energies of 10.64 and 10.03 eV. Helium-neon mixtures will produce a resonance energy of 10.97. For a mixture of BF₃ in NO₂, helium-xenon gas is ideally suited in that the ionization potential of NO₂ is above the resonance of xenon yet the ionization potential of BF₃ is below. BF₃ is selectively ionized while NO₂ is not ionized.

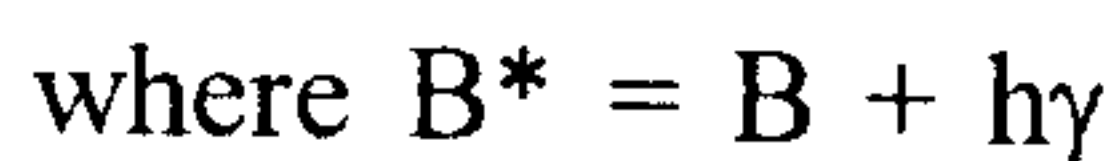
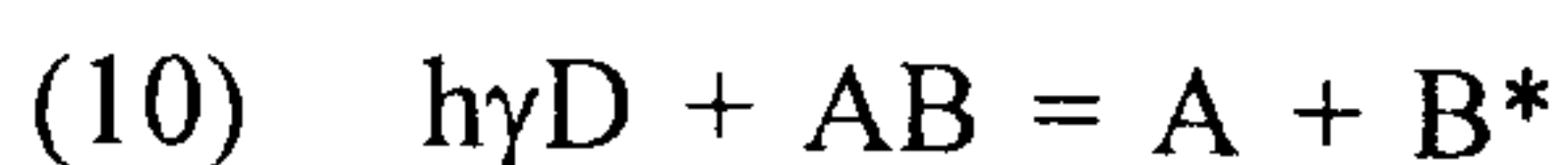
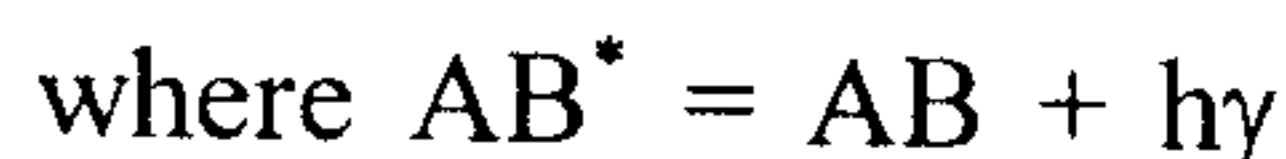
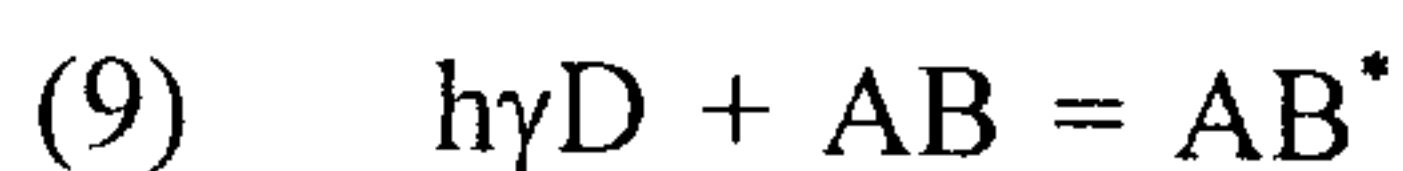
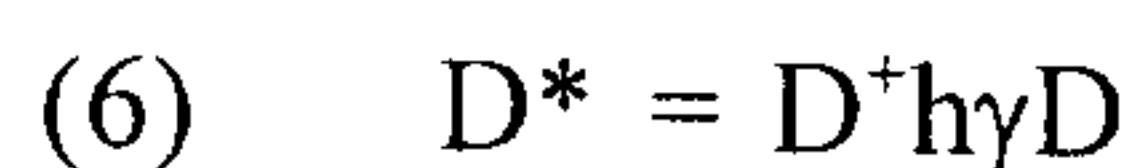
Referring to FIG. 5, a pulsed capture detector (PCD) has cylindrical housing 312 around cylindrical member 314. Passage 316 delivers helium from a source 318 through a valve 319 and regulator 321 slightly above atmospheric pressure. The helium flow is into manifold 323 threaded to a detail 320 in a fitting body 322. Dopant Ne, Xe, Kr and Ar tanks 350, 352, 354 and 356 are connected through valves 360, 362, 364 and 366 and pressure regulators 370, 372, 374, and 376. Valve 319 and a selected solenoid valve mix helium and rare gas Ne, Xe, Kr or Ar at the manifold 323 which flows between the electrodes 324 and 326 across the gap 325 and exposed to the spark from the DC pulse circuit 327.

The flow passage 316 connects downstream with a larger axial hollow passage 328. Rings 334 and 335 are positioned axially along passage 328. Ring 334 has a bias voltage and also serves as a first terminal for the electrometer 336. The bias is about -50 VDC to -400 VDC; and -200 VDC is illustrative. The ring 335 is the second terminal for the electrometer 336 to measure current from the ionization of the trace compounds by the excited dopant. Recorder 338 forms a record of the ionization current measuring the trace compound. The injection tube 340 provides sample gas supplied from the GC column 348. The injector tube 340 is coaxially centered within the exhaust passage 344 which connects with passage 328 through a fitting 342 like the fitting 322. A smaller fitting 346 is centered in the fitting 342.

Doped carrier gas flows from top to bottom while sample gas from the GC column 348 enters through the injector tubes 340. The sample and carrier gas (with dopant) commingle. Trace

compounds are ionized and electrometer 336 measures trace concentration. The carrier gas flow is substantially greater than the sample flow. The commingled and reacted sample and carrier gas is exhausted through the outlet 344.

Helium and the dopant flow into the PCD through fitting 320 into the spark gap 325 where ions and atoms in the excited state are formed. The dopant "D" is energized and excited to emit photons. Using argon as an example, emission forms resonance lines at 104.8 and 106.6 nm with corresponding energies of 11.62 and 11.83 eV, respectively. Helium containing D* gas mixes with AB from the tube 340. D* emits the photon $h\nu$ in proximity to compound AB and reactions are:



where $h\nu$ denotes photon emission of excited dopant D*. (9) and (10) reactions form specific and characteristic emission spectra, thereby enabling identification and quantification. Equations (7) and (8) describe reactions which produce free electrons measured with electrometer 336 where electron current measures concentration of compound AB.

The present invention selects the dopant D thereby allowing selected ionization of components of the sample gas. If $D = Ar$ and $D^* = Ar^*$, then Ar^* radiation is $h\nu_{Ar} = 11.62$ and 11.83 eV and will not ionize any compound with an ionization potential above 11.83 eV. Air is not ionized by the Ar^* source while air pollutants with ionization potentials below 11.83 eV are ionized. One example comprises air with an impurity such as carbon tetrachloride (CCl_4).

In another example, NO_2 has impurity of BF_3 . If $D = \text{Xe}$, Xe exhibits a resonance energy at 9.57 eV. The ionization potential of NO_2 is 9.75 eV which is above the resonance energy of Xe while the ionization potential of BF_3 is 9.25 eV which is below the resonance of Xe. BF_3 in the NO_2 is selectively ionized while NO_2 is not ionized. The electrometer 336 measures trace concentrations of BF_3 . Ar, Kr and Ne are not suitable dopants since the resonance energies are greater than the ionization potential of NO_2 ; therefore the NO_2 as well as the BF_3 would be ionized by these dopants.

In the passage 328, the radiation from the excited dopant is absorbed by the analyte and those components with ionization potentials less than the resonance energy of the selected dopant are current detected by the collecting electrode 335 and measured by the electrometer 336.

Fig. 6 shows selected ionization concepts where the axis 380 represents dopant emission radiation $h\nu_D$ in electron volts (eV). The line 382 locate the Ar emissions at 11.62 and 11.83 eV. The line 386 represents the 10.97 eV emission from Ne and the line 388 represents the 9.57 eV emission from Xe. Finally, emissions 384 are 10.03 and 10.64 from Kr. Ionization potentials are depicted on the axis 390. The line 392, 394, 396 and 398 represent the ionization potentials of air constituents O, H_2O , CO_2 and N, respectively. The ionization potential 393 of CCl_4 is 11.47 eV. NO_2 and BF_3 potentials are 395 and 397, respectively.

For dopant emission photon $h\nu_D$, any element or compound which is on the high energy side of $h\nu_D$ (that is, to the right of the emission line in Fig. 6) is ionized while any element or compound which falls to the low energy side of $h\nu_D$ (that is, on the left of the emission line) will not be ionized. Dopant gases are selected based upon two criteria which are (1) the ionization potential of the compound to be measured and (2) the ionization potentials of other constituents not measured which generate "noise" in the measure of the compound of interest.

In operation, selected dopants are introduced into the carrier gas by the solenoid valve from the reservoir of the selected dopant gas. If Xe is the dopant, solenoid valve 362 allows Xenon from the reservoir 352 to flow through the pressure regulator 372 to the manifold 323.

FIGURE 7

Four detector chambers 451, 453, 455 and 457 receive GC column 448 flow from the GC conduit 472 to a valve 470 which "splits" the flow into four parts. Conduits 440 connects to four ionization detectors chambers 451, 453, 455 and 457. Four different carrier gas sources 450, 452, 454 and 456 flow into the detector chambers. Gas constituents are excited and commingled with the sample gas splits. The excited carrier gases ionize the sample, generating an ionization current. Mixtures of carrier and sample gas are vented from each chamber through a port 444. Ionization currents generated at chambers 451, 453, 455 and 457 are transferred to the computer 460. Measurements processed at the computer 460 yield identity and concentrations of the sample gas. Results from the computer go to a recorder 438. The number of detectors can be varied. In analyzing a large number of different compounds, accuracy and precision may be maximized by using more detectors.

FIGURE 8

The pulsed discharge photoionization capture detector (PDPID) has a long cylindrical housing 512 which contains a cylindrical member 514 which is axially hollow at 516. The helium source 518 flows through a valve 519 and regulator 521 to deliver helium at a pressure slightly above atmospheric. Manifold 523 via fitting 520 connects to a fitting 522 at the body 512 of the PDPID. Reservoir 566 is connected through valve 564 and pressure regulator 562 to the manifold 523. By opening valves 519 and 564, helium and dopant gas flow to the manifold 523 and into the axial passage 516 and between the electrodes 524 and 526.

5 The electrodes 524 and 526 are about 1/16" with spaced end faces approximately 1/16" across passage 516. Electrodes 524 and 526 are electrically insulated from the PDPID. The electrode 526 is grounded while the electrode 524 is provided with a high voltage pulse of short duration by the DC source 527. The two terminals 524 and 526 form a sharply fixed, narrowly constrained spark so that the spark does not dance around the two electrode faces and remains a straight line.

10 Carrier gas is introduced into the PDPID from top to bottom. Sample gas from the GC column 548 enters the passage 528 through the injector tube 540 so that sample and carrier gas excited by the spark commingle. Compounds are ionized producing a response across the exposed rings 534 and 535 input to the electrometer 536 indicative of the sample and concentration. After commingling and reacting, the mixture of sample and carrier gas is swept from the passage 528 of the PDPID and exhausted through the outlet 544. The outlet is supported in the fitting 546 in the end cap 542. The GC gas flow input is the tube 535.

15 Helium and a dopant gas flows into the PDPID through fitting 520 and into the spark gap 525 where ions and atoms are in the excited state. Dopant "D" is energized and excited. The excited dopant passes from the spark gap 525 through passage 516 into the passage 528 of the PDPID. Dopant D in the excited state emits photons. Using argon as an example dopant, emission resonance lines at 104.8 and 106.6 nm have energies of 11.83 and 11.62 eV, respectively. By mixing dopant D with helium and exciting the gas at the gap 525, excited

dopant D* is created. D* decays within approximately 5 microseconds after excitation. Some photons from decay pass through channel 516 into channel 528. Sample AB is injected into the channel 528 and exposed to photons h ν D resulting from the decay of D*. Flow of carrier and sample gas is from top to bottom to the outlet 544. Reactions are exemplified in Equations (1) to (10) above.

Table 1 summarizes emission spectra from helium, argon and krypton doped helium. Other gas mixtures can be effectively used and the data primarily support the examples presented.

TABLE 1
EMISSION SPECTRA FROM HELIUM AND ARGON AND KRYPTON DOPED HELIUM

ACTIVE SPECIES	WAVELENGTH (nm)	ENERGY (eV)
He	388	
He ₂	70 - 90	13.5 - 17.7
Ar	104.8	11.83
Ar	106.6	11.62
Kr	116.5	10.64
Kr	123.6	10.03
Ar ₂	121 - 133.6	9.28 - 10.24
Kr ₂	139.7 - 152.8	8.11 - 8.87

The sample gas may be split and passed through multiple detectors. Electrometer output current with helium as a carrier gas, C_{He}, is measured and stored within the computer 560. The electrometer outputs C_{He} + Ar and C_{He} + Kr from the second and third detectors, respectively, are measured simultaneously and likewise stored within the computer 560.

The ratios

$$(11) R'_{Ar} = C_{He+Ar} / C_{He}$$

5 and

$$(12) R'_{Kr} = C_{He+Kr} / C_{He}$$

are computed. The system is first "calibrated" by measuring the
10 ratios R'_{Ar} and R'_{Kr} using a calibration gas comprising a known
amount of benzene. All other constituents exhibit ionization
potentials above the highest emission level of the carrier gas and,
therefore, do not contribute to the electrometer current readings of
the detectors. The ratios defined in equations (11) and (12) for
15 benzene gas are R''_{Ar} and R''_{Kr} , respectively. Ratios measured using
the unknown sample, normalized to a corresponding reading for
benzene of 100, are computed from the equations

$$(13) R_{Ar} = 100 (R'_{Ar} / R''_{Ar})$$

20 and

$$(14) R_{Kr} = 100 (R'_{Kr} / R''_{Kr})$$

Table 2 lists normalized ratios R_{Kr} and R_{Ar} for selected
25 compounds. The tabulation is presented for illustration only. If an
unknown sample gas R_{Ar} is measured at 77.8 ± 0.8 , the designated
uncertainty is attributed to random errors. In Table 2, the
compounds $C_3H_7NO_2$ ($R_{Ar} = 78.3$) and CH_3CHO ($R_{Ar} = 77.9$) and 1-
pentene ($R_{Ar} = 77.6$) all fall within the uncertainty of ± 0.8 . With
30 only two detectors, the unknown compound could not be uniquely
identified from ionization detection measurements. Assume that R_{Kr}
is 37.4 ± 0.4 . From Table 2, only 1-pentene is within the range of
values of R_{Ar} and R_{Kr} since the tabulated values of R_{Kr} for $C_3H_7NO_2$
and CH_3CHO are 0.74 and 43.4, respectively. The unknown
35 compound is, therefore, identified as 1-pentene. The concentration

of 1-pentene is from C_{Ar} or C_{Kr} standardized with a calibration gas containing 1-pentene.

Computations are performed in real time with the computer 560. The identification analysis is depicted graphically in Fig. 9A. R_{Ar} is plotted on the axis 584 and R_{Kr} is plotted on the axis 582. Corresponding "coordinates" for 1-pentene, $C_3H_7NO_2$ and CH_3CHO , with expected systematic uncertainties for each value, are taken from Table 2 and depicted as circles 572, 574 and 570, respectively. Should R_{Ar} and R_{Kr} plot within any circle of uncertainty, the unknown compound is thereby identified. In the previously discussed example, the measured values of R_{Ar} and R_{Kr} plot within the circle 572 and therefore the unknown compound is identified as 1-pentene.

TABLE 2
NORMALIZED RESPONSE RATIOS R_{Ar} AND R_{Kr} FOR SELECTED COMPOUNDS

COMPOUND	R_{Ar}	R_{Kr}
CS ₂	204.0	38.3
1-hexene	81.7	41.8
C ₃ H ₇ NO ₂	78.3	0.74
CH ₃ CHO	77.9	43.4
1-pentene	77.6	37.4
2-methyl-1-pentene	76.0	35.3
heptane	76.0	4.58
1-butene	70.5	24.3
butane	62.4	1.13
n-C ₃ H ₇ OH	60.9	10.2

As a second example, assume that R_{Ar} is measured to be 76.8 +/- 1.0 and R_{Kr} is measured to be 36.0 +/- 2.0. The illustrative uncertainties are greater than usual. From Table 2, it is not possible to define uniquely the unknown compound as 1-pentene or 2-methyl-1-pentene since both fall within the uncertainty ranges. An additional detector with gas dopant helps so that the normalized

ratio from this detector, denoted as " R_x ", delineates between the two compounds in question. The data using four detectors (which yields three ratios) is depicted graphically in Fig. 9B. Coordinates representing 1-pentene and 2-methyl-1-pentene, with spheres representing the systematic uncertainty of the system, are depicted as 592 and 590, respectively. R_{Kr} and R_{Ar} are plotted along the axes denoted by the numerals 582 and 584, respectively. The ratio from the additional detector, R_x , is plotted along the axis denoted by 586 and is in arbitrary units. Hypothetical values for R_x 1-pentene and 2-methyl-1-pentene, (for purposes of illustration), are denoted by the numerals 596 and 595, respectively. Should values of R_{Ar} , R_{Kr} and R_x for an unknown plot within the sphere of uncertainty for either compound, the unknown compound is identified. The graphical interpretation is presented only for purposes of illustration and is easily adapted for computer interpretation.

FIGURES 10, 11 AND 12

The circular detection system 620 utilizes a carrier gas source 612 connected to the detector valve 613. The circular detector 620 in a representative GC system utilizes a sample source 611 connected with the loading valve 613. They provide a carrier gas flow to a GC column 615. System timer 616 controls operation. Compounds supplied with the flowing carrier gas flow through the valve 613 to the GC column 615. There is a tangential inlet port 618 to the detector interior to sustain rotational motion and discharge through a vent port 619. The collecting electrode terminal 621 is connected to the electrometer 628. The terminal 621 connects with one ring electrode while the terminal 622 connects with a bias electrode. A B+ supply 634 provides power. One output from the B+ supply 634 is to the timer 616 and then to a charging circuit 642. The charging circuit operates with a high voltage discharge circuit 643 to form an output pulse having a controlled polarity, controlled width and specified current flow. This is input at a first terminal 624 opposite a ground terminal 625. The terminals 624 and 625 provide the DC spark in the detector 620. One of the two terminals is hollow for delivery of helium from a helium source 626.

A window 627 passes light to be emitted from the spark, and observed by a spectrum analyzer 640. The analyzer 640 provides an output signal to the recorder 641. Helium is delivered at the center of the detector 620 through the hollow electrode 624 from the reservoir 626. Dopant may be optionally introduced from the reservoir 626' into the helium flow.

The detector housing 620 has two cylindrical shell portions. One shell portion 629 incorporates a circular protruding lip which enables the shell half 629 to join with a second shell portion 631. The shell portions 629 and 631 join with an overlapping lip arrangement so that a chamber 632 is formed. The collecting electrode 621 is connected to a ring 633 while the similar ring 635 is the bias electrode. The housing portions 629 and 631 are formed of a material which is not an electrical conductor. In Fig. 12, the shell portion 629 is provided with a tangentially located inlet passage 618 to introduce gas flow at the interior tangential edge of the cylindrical chamber. The port 619 is a vent located radially inwardly.

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FIGURE 13

The numeral 710 identifies the gas sampling apparatus formed of an insulating material. The body 710 is divided into two chambers by the partition or "window" 740 forming the upper spark chamber 712 which is leak proof to the surrounding atmosphere and a lower sample chamber. Two round and equal diameter electrodes 714 and 716 protrude inwardly from the body 710 of the detector. The spark gap 715 within the spark chamber 712 has an insulating material at the faces of the electrodes 714 and 716 sufficiently thick to physically isolate the electrodes from the environs of the interior of spark chamber 712 yet sufficiently thin to allow the generation of a pulsed DC spark across the spark gap 715. Electrode 716 is electrically connected to B+ voltage power supply 720 while the electrode 714 is grounded at 722. The voltage applied to the electrode pair is timed by a clock 738. The spark chamber 712 is filled with helium and a trace of krypton.

Sample gas enters the sample chamber through a port 726 and exits the chamber through the port 728. A small pump delivers sample gas. The sample chamber contains circular electrodes 730 and 732 recessed within the chamber walls and exposed to the interior of the chamber. Electrode 732 is grounded at 734. The electrode 730 is connected to an amplifier 737 and then to the recording device 736. A clock 738 controls the applied positive or negative voltage and times the recorder. The electrode 732 has the requisite voltage to attract desired charged particles within sample chamber. The window 740 separating the spark chamber 712 and the sample chamber is a thin membrane of magnesium fluoride (MgF_2) or lithium fluoride (LiF). The material and dimensions are selected so that photoemissions at the desired energy levels experience minimal absorption entering into the sample chamber. The discharge heats the gas in the spark gap 715. Heated relatively buoyant gas in the spark path rises in the closed spark chamber 712 where it is cooled by mingling with cooler gas. Simultaneously, cooler gas replaces the heated gas at the spark gap 715. The net result is circulation within the closed spark chamber 712 as depicted by the broken lines 718. Convective circulation constantly supplies "fresh" gas to the spark gap 715.

Krypton in the excited state emits photons at 116.5 and 123.6 nanometers (nm) with corresponding energies of 10.03 and 10.64 electron volts (eV), respectively. This radiation passes through the window membrane 740 and into the sample chamber where it interacts with the sample gas. Each spark creates a fresh supply of Kr^* which, in turn, decays to the ground state by the emission of 10.03 eV and 10.64 eV photons. The spark generation system in cooperation with the helium-krypton gas mixture acts as a self replenishing source of 10.03 eV and 10.64 eV radiation.

Sample flow is preferably continuous although discrete samples may be taken. In air monitoring, small concentrations of pollutant compounds AB and air are exposed to the photon flux of energies 10.03 and 10.64 eV from the spark chamber 712 through window membrane 740. This photon flux ionizes the compound AB. Free electrons are collected at the electrode 730 which is at a

positive potential. Electrode 732 is at ground to retard ionic recombination and to repel electrons. The free electron current from the electrode 730 is recorded by the recorder 736 with the current proportional to the concentration of AB. Electron current is,
5 therefore, an analytical measure of concentration.

Recall that Kr* emits radiation at 10.03 and 10.64 eV. This radiation will not ionize any compound with an ionization potential above 10.64 eV. Major constituents of air are not ionized by the emissions from Kr*, but impurities in the air sample
10 (pollutants with ionization potentials below 10.64 eV) will be ionized.

While the foregoing describes the embodiments of the present invention, the scope is determined by the claims.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A method for analyzing a sample compound in a carrier gas comprising the steps of:

(a) through a first inlet, flowing said carrier gas through a chamber for exposure to pulsed DC current across the chamber;

(b) energizing at least one component of said carrier gas to an excited state as a result to exposure to said pulsed DC current;

(c) flowing a gaseous sample compound into said chamber through a second inlet downstream from said first inlet and downstream from said pulsed DC current thereby commingling said gaseous sample compound with said carrier gas;

(d) forming charged particles in the gaseous sample as a result of ionizing radiation emitted in the decay of said excited component of said carrier gas wherein the charged particles are formed from said gaseous sample;

(e) measuring said charged particles wherein said measurement occurs in timed relationship with respect to said pulsed DC current; and

(f) selectively determining types and concentrations of compounds contained in said gaseous sample by utilizing said measurements.

2. The method of claim 1 wherein said carrier gas comprises argon.

3. The method of claim 2 wherein helium is the larger component and argon is the smaller component of said carrier gas.

4. The method of claim 1 wherein said ionizing radiation is below the threshold energy level of air.

5. A method of analyzing a sample compound comprising the steps of:
 - (a) flowing a carrier gas through a chamber for exposure to DC current thereby energizing at least one component of said carrier gas to an excited state as a result of exposure to said DC current;
 - (b) commingling a gaseous sample with said carrier gas within a chamber wherein said carrier gas comprises at least one component in an excited state;
 - (c) forming one or more excited compounds in said gaseous sample resulting from photon emission in the decay of at least one excited component of said carrier gas wherein the emissions involve an energy exchange up to about 11.8 eV; and
 - (d) determining the type and concentration of one or more compounds in said gaseous sample by measuring photon emission from the decay of said excited compounds in said gaseous sample.
6. The method of claim 5 wherein one component of said carrier gas is argon.
7. The method of claim 6 wherein said observation is made during DC current flow.
8. The method of claim 6 wherein said observation is made in a region of said chamber not including said current flow.
9. The method of claim 8 wherein the carrier gas comprises helium and argon, and the observed optical emissions are induced by ionizing radiation emitted by argon which is energized to a metastable state.

10. A gas detector for identification and quantification of sample compounds, comprising:

(a) an elongated chamber having a first chamber inlet at one end and an outlet at the other end, and a gas flow path between said first inlet and outlet ends;

(b) two electrodes spaced apart and located to produce short, repeated, high voltage, pulsed DC current within said chamber across said gas flow path and wherein spark duration minimizes electrode erosion and permits observation of phenomena occurring at and between said DC current at and remote from said electrode location;

(c) means for introducing a carrier gas into said chamber through said first chamber inlet and flowing said carrier gas in said gas flow path;

(d) means for introducing a sample gas into said chamber through a second inlet which is located downstream from said first chamber inlet and downstream from said two spaced electrodes, and flowing said sample gas in said gas flow path; and

(e) wherein ions are produced by said spark or by metastable species of said carrier gas.

11. The apparatus of claim 10 wherein a potential gradient is created between said spark electrodes and a collector electrode in said chamber for the measurement of ionization.

12. The apparatus of claim 11 wherein a series of electrodes provides a focusing electrical gradient to control and measure the mobility of ions formed by said spark.

13. A method of selectively analyzing a sample of air for impurities comprising the steps of:

(a) flowing a carrier gas comprising argon through a chamber for exposure to periodically pulsed DC currents across said chamber;

(b) energizing said argon to an excited metastable state as a result of exposure to said current;

(c) commingling an air sample with said carrier gas within said chamber by inputting said air sample into said chamber downstream from the input of said carrier gas and downstream from said periodically pulsed DC current across said chamber;

(d) forming charged particles as a result of ionizing radiation emitted by the decay of said argon component of said carrier gas in said chamber, and wherein the charged particles are formed by selective ionization of impurities of said air sample based on ionization potentials of said impurities while precluding ionization of major constituents of air; and

(e) observing reactions induced by ionizing radiation produced by the decay of said metastable argon with said impurities of said air sample.

14. The method of claim 13 wherein said impurities are identified and quantified by measuring charged particles resulting from the ionization of impurities produced by ionizing radiation emitted by the decay of said metastable argon.

15. The method of claim 13 wherein said impurities are identified and quantified by observing spectral emission of impurities induced by ionizing radiation from the decay of said metastable argon.

16. The method of claim 13 wherein said observations are made during said spark discharge.

17. The method of claim 13 wherein said observations are made remote from said spark gap and at a time following said spark discharge.

18. The method of claim 13 wherein impurities with ionization potentials below approximately 11.8 eV are observed.

19. The method of claim 13 wherein the major constituent of said carrier gas is helium and the second constituent is argon in a concentration of approximately 0.3%.

20. A method of testing an airborne sample comprising the steps of:

- (a) providing an airborne sample flowing through a test chamber;
- (b) simultaneously providing a carrier gas flowing through said test chamber;

- (c) within said test chamber, forming with an electrical current a metastable species in said carrier gas wherein said metastable species is characterized by having a ground energy state and excited state of sufficient time duration to enable an energy transfer from said excited state of said metastable species to said airborne sample by the emission of photons; and

- (d) wherein the excited state causes an energy transfer to said airborne sample wherein the excitation energy range of said metastable species is selected to preclude energizing the constituents of air.

21. The method of claim 20 wherein air constituents of nitrogen, oxygen, water vapor and carbon dioxide are not energized.

22. A method for analyzing a sample compound in a carrier gas, comprising the steps of:

- (a) through a first inlet, flowing said carrier gas through a chamber for exposure to pulsed DC current across said chamber wherein said carrier gas comprises argon;
- (b) energizing at least one component of said carrier gas to an excited state as a result of exposure to said pulsed DC current;
- (c) flowing a gaseous sample compound into said chamber through a second inlet downstream from said first inlet and also downstream from said pulsed DC current thereby commingling said gaseous sample with said carrier gas;
- (d) forming charged particles in the gaseous sample as a result of ionizing radiation emitted in the decay of said excited component of said carrier gas wherein said charged particles are formed from said gaseous sample;
- (e) measuring said charged particles wherein said measurement occurs in timed relationship with respect to said pulsed DC current; and
- (f) selectively determining types and concentrations of compounds contained in said gaseous sample by utilizing said measurements.

23. The method of claim 22 wherein helium is the larger component and argon is the smaller component of said carrier gas.

24. The method of claim 23 wherein said ionizing radiation is below the threshold energy of air.

25. A method for analyzing a sample compound comprising the steps of:

(a) flowing a carrier gas comprising argon through a chamber for exposure to DC current thereby energizing at least one component of said carrier gas to an excited state as a result of exposure to said DC current;

(b) commingling a gaseous sample with said carrier gas within said chamber wherein said carrier gas comprises at least one component in an excited state;

(c) forming one or more excited compounds in said gaseous sample resulting from photon emission in the decay of at least one excited compound of said carrier gas wherein emissions involve energy exchange up to about 11.8 eV; and

(d) determining the type and concentration of one or more compounds in said gaseous sample by measuring photon emission from the decay of said excited compounds in said gaseous sample.

26. The method of claim 25 wherein said observation is made during the DC current flow.

27. The method of claim 25 wherein said observation is made in a region of said chamber not including said DC current flow.

28. The method of claim 27 wherein the carrier gas comprises helium and argon, and the observed optical emissions are induced by ionizing radiation emitted by argon as said argon decays from a metastable state.

29. An electron capture detector comprising:
- (a) a closed chamber having a helium flow inlet and spaced helium flow outlet to enable helium flow therethrough;
 - (b) spaced electrodes cooperating with a DC current source thereby permitting an electrical arc to be formed between said spaced electrodes defining a spark thereacross, said spaced electrodes being positioned in said chamber to form a spark gap across said helium flow through said chamber;
 - (c) a dopant gas source connected to said chamber to provide a controlled dopant flow at continuously adjustable locations within said chamber thereby forming a base current within said chamber where said base current is initiated by said spark across said spark gap;
 - (d) a sample gas source connected to said chamber to provide sample gas containing eluted compounds of unknown concentration;
 - (e) current detector electrode means spaced along the axis of said chamber for collection of current formed as a result of said spark across said spark gap wherein said helium flow moves toward said current detector electrodes to enable currents to be formed and measured indicative of one or more said eluted sample compound concentrations in said chamber and dependent on the dopant gas in said helium; and
 - (f) wherein said current detector electrode means measures the eluted sample concentrations in said chamber by changes in said current flow.

30. The apparatus of claim 29 wherein the dopant gas is hydrogen.

31. The apparatus of claim 29 wherein said current detector electrode means are axially spaced downstream from said spark gap formed by said spaced electrodes.

32. The apparatus of claim 29 wherein said dopant gas is introduced into said chamber by a dopant gas tube with one end of said dopant gas tube connected to a source of dopant gas external to said chamber and the second open end of said dopant gas tube terminating within said chamber downstream of said spaced electrodes which form said spark gap.

33. The apparatus of claim 32 wherein said chamber encloses an open end of said dopant gas tube at a location therein so that said helium flow mixes with the dopant gas and said dopant gas forms an electrical current resultant from the spark at said spaced electrodes.

34. The apparatus of claim 33 wherein said chamber is constructed with an elongate helium gas flow passage and said passage directs helium flow to said current electrode detector means and also directs photon emissions from said spark to interact with dopant gas to form an electrical current.

35. The apparatus of claim 34 including a sample source external to said chamber and a sample carrier gas tube positioned in said chamber and concentric with said dopant gas tube, and wherein helium gas flow is from said inlet to said outlet; and

wherein the opening of said dopant gas tube is positioned to introduce dopant gas downstream of said spaced electrodes which form said spark gap and wherein the opening of said sample carrier gas tube is downstream of the opening of said dopant gas tube so that said dopant gas flows downstream to mix with said eluted sample and sample gas carrier.

36. The apparatus of claim 35 wherein said chamber is an elongate, open, hollow passage in a surrounding housing, and said dopant gas tube is located in said chamber.

37. The apparatus of claim 34 wherein the axes of said source carrier gas tubes and said dopant gas tubes are parallel within said chamber and said axes are essentially parallel to the axis of said chamber.

38. A method of measuring an eluted sample from a GC column sample source comprising the steps of:

- (a) flowing an inert gas from an inlet to an outlet in a chamber through a spark gap positioned near said inlet;
- (b) forming a spark to excite the inert gas, said spark being formed by an electrical discharge across two electrodes which cooperate with a pulsed DC source and are spaced to form a spark gap;
- (c) at continuously adjustable locations downstream in said chamber, introducing a dopant gas into said inert gas flow to enable said dopant gas to respond to the excited inert gas and thereby form an electric current flow in said chamber;
- (d) further downstream from the point of introduction of said dopant gas in said chamber introducing an eluted sample from a sample source which is mixed with said inert gas and said dopant gas to cause a variation in said electric current flow in said flowing gases related to eluted sample quantity; and
- (e) determining the concentration of said eluted samples from a measure of said electric current flow.

39. The method of claim 38 further including the step of measuring current flow solely from dopant gas flow to obtain a base current measurement, and then measuring current reduction resultant from eluted sample.

40. The method of claim 39 further including the step of measuring current associated with an eluted sample in said chamber, and then measuring associated current flow with a subsequent eluted sample in said chamber.

41. The method of claim 40 wherein the step of measuring current includes the initial step of positioning current responsive electrodes in said chamber at a selected downstream location so that current is measured.

42. The method of claim 41 including the step of measuring current between two measuring electrodes in said chamber.

43. The method of claim 42 wherein the dopant gas is hydrogen, and the dopant gas reacts with photons emitted resulting from the spark to create a current flow in the dopant gas in said chamber.

44. The method of claim 43 wherein spark emitted photons are directed by said chamber into the dopant gas to disassociate electrons to create the current flow.

45. A charged particle detector comprising:

(a) a closed chamber having an inert gas flow inlet and spaced outlet to enable gas flow therethrough;

(b) spark forming electrodes cooperating with a pulsed DC current source thereby forming a spark sufficient to enable an electrical arc to be formed between said electrodes defining the spark thereacross, said electrodes being positioned in said chamber to form a spark gap across inert gas flow through said chamber;

(c) spaced detector means downstream in said chamber for collection of current formed as a result of the spark across the gap wherein the inert gas flow moves toward said detector means and a current is formed indicative of eluted sample concentration introduced, from an external source, into said chamber downstream from said spark forming electrodes;

(d) a voltage source connected to said detector means to provide a controlled voltage thereto for enabling said detector means for current detection; and

(e) wherein the detector means quantifies the eluted sample in said chamber by measuring said detected current.

46. The apparatus of claim 45 wherein the inert gas is helium.

47. The apparatus of claim 45 wherein said detector means is spaced remotely from said spark forming electrodes in said chamber.

48. The apparatus of claim 45 wherein said spark forming electrodes in cooperation with said pulsed DC current source form an incandescent current flow across said gap, and said spark forming electrodes are flush mounted in a surrounding circular ring of non conductive material to enable gas flow through the spark.

49. A method of analyzing an eluted sample compound in a carrier gas comprising the steps of:

(a) flowing the carrier gas through a chamber for exposure to a spark discharge across the chamber, said spark discharge being formed across a pair of spark forming electrodes cooperating with a pulsed DC current source; and

(b) introducing an eluted sample into said carrier gas downstream from said spark discharge and observing downstream in the chamber spark caused current flow in the chamber to analyze the concentration of said eluted sample compound flowing through the chamber by detecting changes in said current flow.

50. The method of claim 49 wherein a spark of DC current flows upstream in the chamber and the carrier gas flows away from the spark for the step of observing.

51. The method of claim 50 wherein the observation of said spark caused current flow is made from a region of the chamber not involving the spark and the current flow is measured by positioning a pair of spaced electrodes in said chamber.

52. A gas detector for identification and quantification of sample compounds, comprising:

- (a) an elongated chamber having a chamber inlet at one end and an outlet at the other end, and a gas flow path between said inlet and outlet ends;
- (b) means for flowing helium in said chamber;
- (c) two electrodes spaced apart and located to produce current spark within said chamber and across said gas flow path and wherein spark interacts with said flowing helium thereby producing photon emissions;
- d) means for introducing sample and sample carrier gas into said chamber at a selected location remote from the electrodes in said chamber;
- (e) spaced detector means downstream in said chamber for measuring current generated by the ionization of said sample by said photon emission;
- (f) means for:
 - (1) identifying said sample by measuring the time at which said measured current flows following said introduction of said sample into said chamber, and
 - (2) quantifying said sample by measuring the magnitude of said current change; and
- (g) means for optimizing said current generated by the ionization of said sample by adjusting said selectable location of said sample and sample carrier gas introduction into said chamber and by adjusting the voltage applied to said spaced detector means.

53. The method of claim 52 wherein said sample and sample carrier gas are from a GC column input to said chamber at a location downstream from said electrodes.

54. The method of claim 52 wherein the helium flow picks up said sample and sample carrier gas flow and mixes therewith so that said sample causes said current to flow in proportion to sample quantity.

55. A charged particle detector comprising:

- (a) a closed chamber having a helium gas flow inlet at a first end and spaced outlet at a second end to enable helium flow therethrough;
- (b) spaced electrodes cooperating with a pulsed DC power supply responsive to DC current flow sufficient to enable an electrical spark to be formed between said electrodes, said electrodes being positioned to form a spark in helium flow into said chamber to thereby create photon emission;
- (c) spaced detector means downstream in said chamber for collection of charged particles downstream of the spark across the gap wherein the charged particles enable a current to be formed indicative of sample gas concentration in said chamber;
- (d) an inlet downstream in said chamber for controllably introducing a sample and carrier gas flow from a GC column at a selected location downstream from said spark forming electrodes so that said sample and carrier gas and said helium flow provide current for said detector means; and
- (h) means for optimizing said current by adjusting said selected location for sample gas and carrier gas introduction and by adjusting voltage applied to said detector means.

56. A method for analyzing a sample compound in a carrier gas comprising the steps of:

- (a) commingling a dopant gas and an inert gas forming a carrier gas and the dopant gas is selected such that the resonance energy of said dopant is greater than the ionization energy of said compound to be measured;
- (b) flowing said carrier gas through a chamber for exposure to DC current across the chamber;
- (c) energizing at least one component of said carrier gas to an excited state as a result of exposure to said DC current;
- (d) commingling said carrier gas with a sample gas comprising one or more compounds;
- (e) forming charged particles within said chamber as a result of ionizing radiation emitted in the decay of said excited component of said carrier gas interacting with one or more compounds contained within said sample gas;
- (f) measuring the electrical current resulting from the flow of said charged particles wherein said measurement step occurs in timed relationship to charge dispersal; and
- (g) selectively identifying the concentrations of one or more said compounds contained in said sample utilizing said current measurement.

57. The method of claim 56 wherein said inert gas is helium.

58. The method of claim 57 wherein the resonance energy of said dopant is less than the constituents¹ of the sample gas which are not to be measured.

59. A method for analyzing a sample compound comprising the steps of:

- (a) flowing a carrier gas through a chamber wherein said carrier gas comprises an inert gas and a dopant gas wherein said dopant gas is selected such that the resonance energy of the dopant component is greater than the ionization potential of the compound to be measured in said gaseous sample;
- (b) commingling a gaseous sample with said carrier gas within a chamber forming a composite gas;
- (c) exposing said carrier gas to a spark generated by DC current; and
- (d) optically observing spark caused emissions in said chamber to analyze said gaseous sample component, wherein said emissions involve an energy exchange up to the resonance energy of said dopant.

60. The method of claim 59 wherein said observation is made during DC current flow.

61. The method of claim 59 wherein said observation is made in a region of said chamber not including current flow resulting from the ionization of compounds within said gaseous sample.

62. The method of claim 61 wherein said observed optical emissions are induced by ionizing radiation emitted by said dopant component decaying from a metastable state, said dopant component being excited to a metastable state by said pulsed DC current.

63. A gas detector for identification and quantification of sample compounds, comprising:

- (a) an elongated chamber having a chamber inlet at a first end and an outlet at a second end, and a gas flow path between said inlet and outlet;
- (b) an input manifold for inserting carrier gas into said flow path of said chamber;
- (c) a reservoir, pressure regulator and valve for supplying inert gas at a controlled rate to said manifold;
- (d) a plurality of reservoirs, pressure regulators and valves for selecting one of a plurality of dopants at a controlled rate to said manifold;
- (e) means for introducing into said chamber said inert gas and said selected dopant which are commingled within said manifold thereby forming said carrier gas;
- (f) means for introducing a sample gas into said chamber and commingling said sample gas with said carrier gas;
- (g) two electrodes spaced apart and located to respond to high voltage DC current resulting in sparks within said chamber across said gas flow path and wherein the duration of said sparks minimizes electrode erosion and permits observation of phenomena occurring at and between said sparks and remote from said electrode location;
- (h) means for measuring electrical currents resulting from ions which are produced by said sparks or by metastable species within said carrier gas; and
- (i) means for converting said observed phenomena occurring at and between said sparks and said measured electrical currents to identify and to quantify selected compounds contained within said sample gas.

64. The apparatus of claim 63 wherein said means for measuring said electrical currents comprises a collector and a bias electrode cooperating with an electrometer.

65. The apparatus of claim 63 wherein said means for introducing said sample gas into said chamber comprises an injection tube entering said chamber through a fitting on said second end of said chamber.

66. A method of selectively analyzing a sample of gas for impurities comprising the steps of:

(a) flowing said carrier gas comprising an inert gas and a selected dopant from a set of at least two dopants through a chamber for exposure to DC current across said chamber thereby energizing molecules of said inert gas to a metastable state;

(b) energizing said selected dopant to an excited state as a result of the decay of said inert gas metastable molecules;

(c) commingling a gas sample with said carrier gas within said chamber;

(d) forming charged particles as a result of ionizing radiation emitted by the decay of said energized dopant component of said carrier gas in said chamber, and wherein the charged particles are formed by selective ionization of impurities of said gas sample based on ionization potentials of said impurities while precluding ionization of major constituents of air; and

(e) observing reactions induced by ionizing radiation produced by the decay of said excited dopants with said impurities in said gas sample.

67. The method of claim 66 wherein said impurities are identified and quantified by the selected type of dopant and by the measured charged particles resulting from the ionization of impurities produced by ionizing radiation emitted by the decay of said selected excited dopant.

68. The method of claim 66 wherein said impurities are identified and quantified by observing spectral emission of impurities induced by radiation from the decay of said excited dopant.

69. The method of claim 66 wherein said observations are made during said spark discharge.

70. The method of claim 66 wherein said observations are made remote from said spark gap and at a time following said spark discharge.

71. The method of claim 66 wherein impurities with ionization potentials below the resonance radiation from said selected dopant are measured.

72. The method of claim 66 wherein the major constituent of said carrier gas is helium.

73. The method of claim 66 wherein said dopants are rare gases.

74. A method of analyzing a sample compound from a sample compound source comprising the steps of:

- (a) through a first inlet, flowing a carrier gas through a chamber for exposure to DC current flowing across the chamber;
- (b) energizing at least one component of the carrier gas to an excited state as a result of exposure to said DC current;
- (c) flowing the carrier gas through the chamber downstream of the DC current;
- (d) introducing a gas sample source gas flow into said chamber through a second inlet downstream from said DC current to thereby commingle the introduced sample flow downstream with the flowing carrier gas;
- (e) adjusting the position of introduction downstream;
- (f) forming charged particles in the introduced gas sample as a result of the excited state of the carrier gas; and
- (g) measuring charged particles resultant from commingling of the introduced gas sample flow.

75. A charged particle detector comprising:

- (a) a circular closed chamber having a gas flow inlet and spaced outlet positioned to direct gas flow through said chamber and said chamber directs the gas flow in a circle therein;
- (b) spaced electrodes provided with a current sufficient to enable an electrical spark to be formed in a gap between said electrodes locating the spark thereacross, said electrodes being positioned to form a spark in gas in said chamber to create charged particles; and
- (c) a spaced detector electrode in said chamber for collection of charged particles wherein the charged particles move to said detector electrode to form a current indicative of a sample gas concentration in said chamber.

76. The apparatus of claim 75 wherein a sample gas is diffused with charged particles in said chamber.

77. The apparatus of claim 76 wherein said gas glow comprises helium atoms having an excited high energy metastable state with transitions to a lower energy state, and thereby interact with the gas sample.

78. The apparatus of claim 75 wherein said detector electrode is spaced circumferentially from said spark forming electrodes and at least one bias electrode is connected to a voltage source to control charged particle impingement thereon.

79. The apparatus of claim 75 wherein said spark forming electrodes are periodically pulsed with DC current to form a DC spark during pulsing wherein the spark forms an incandescent current flow across said gap, and said spark electrodes are flush mounted in a surrounding circular housing of non-conductive material to direct gas flow in circular movement.

80. The apparatus of claim 75 wherein said chamber is cylindrical and a gas sample is introduced at a tangent to initiate gas flow.

81. A gas detector for identification and quantification of sample compounds, comprising:

- (a) a circular chamber having a tangential chamber inlet and a tangential outlet, and a circular gas flow path between said inlet and outlet ends;
- (b) means for flowing an inert gas into said chamber;
- (c) two spaced electrodes located in said chamber to produce repeated current sparks across said chamber wherein gas interaction forms energized particles in the chamber;
- (d) a sample source connected to deliver gas into said chamber; and
- (e) means responsive to interacted sample gas and charged particles to enable sample gas detection in said chamber.

82. The apparatus of claim 81 wherein a dopant is added into the chamber by a dopant supply means to provide a source of thermalized electrons to measure electron capture.

83. An electron capture detector comprising:

- (a) a closed chamber having a helium flow inlet to enable helium flow therethrough;
- (b) spaced electrodes forming a spark between said electrodes defining a spark thereacross, said electrodes being positioned in said chamber to form a spark through helium in said chamber;
- (c) a sample gas source connected to an inlet to said chamber to provide sample gas flowing in said chamber and said chamber and said inlet are constructed and arranged to flow gas in a circle in said chamber;
- (d) a spaced detector in said chamber for collection of current formed as a result of the spark across the gap wherein the spark irradiated helium enables a current to be formed indicative of eluted gas sample concentration in said chamber; and
- (e) wherein the detector measures the gas sample in said chamber by change in current flow.

84. The apparatus of claim 83 wherein said chamber is a circular hollow chamber enabling circular flow.

85. The apparatus of claim 84 wherein said chamber is defined by a pair of facing

housing walls extending to a circular, surrounding wall.

86. The apparatus of claim 85 including a tangential flow passage into said circular chamber.

87. A method for analyzing a sample gas comprising the steps of:

(a) serially forming a plurality of carrier gases wherein at least one of said carrier gases comprises an inert gas and a dopant gas selected from a set of dopant gases;

(b) flowing a current through said carrier gases;

(c) energizing at least one component of said carrier gases to an excited state as a result of exposure to said current flow;

(d) mixing a sample gas comprising one or more compounds with said energized carrier gases;

(e) forming charged particles of said sample gas as a result of ionizing radiation emitted in the decay of said excited component of said carrier gases interacting with one or more compounds contained in said sample gas;

(f) measuring the electrical currents resulting from the flow of said charged particles wherein said measurement step occurs after forming charged particles; and

(g) selectively identifying one or more said compounds contained in said sample utilizing said current measurements.

88. A method for analyzing a sample gas comprising the steps of:

(a) forming a plurality of carrier gases wherein at least one of said carrier gases comprises an inert gas and a dopant gas;

(b) providing a detector chamber for each of said plurality of carrier gases;

(c) flowing each of said carrier gases through said provided detector chamber for exposure to said current flow;

- (d) energizing, within each said provided detector chamber, at least one component of each of said carrier gases to an excited state as a result of exposure to said current flow;
- (e) providing a sample gas comprising one or more compounds;
- (f) splitting said sample gas into portions thereby forming sample gas splits for flowing into each said provided detector chamber;
- (g) exposing said sample gas splits to said energized carrier gases within each said provided detector chamber;
- (h) forming charged particles within each said provided detector chamber as a result of ionizing radiation emitted in the decay of said excited components of said carrier gases interacting with one or more compounds contained within said sample gas splits;
- (i) measuring the electrical currents resulting from the flow of said charged particles within each said provided detector chamber thereby forming a set of electrical current measurements; and
- (j) identifying one or more compounds within said sample gas by utilizing said set of electrical current measurements and a predetermined relationship between said measured current set and the identity of said compounds.

89. The method of claim 88 wherein said dopants are selected such that the resonance energy of each of said dopant is different.

90. The method of claim 89 wherein said dopants are selected such that the resonance energy of at least one dopant is greater than the ionization energy of each said identified compounds within said sample gas.

91. The method of claim 90 wherein said electrical current measurements are made simultaneously within each of said provided detector chamber.

92. The method of claim 91 wherein said electrical current measurements are made during said current flows within each provided detector chamber.

93. The method of claim 91 wherein said electrical current measurements are made after the termination of said current flows within each provided detector chamber.

94. The method of claim 91 wherein said electrical current measurements are made in regions of said provided detector chambers remote from said current flow.

95. The method of claim 87 wherein the major constituent of said carrier gases is helium.

96. The method of claim 87 wherein said dopants are rare gases.

97. A gas detector for identifying compounds in a sample gas, comprising:

(a) a plurality of chambers with each chamber having an inlet at a first end and an outlet at a second end, and a gas flow path between said inlet and outlet;

(b) a source of carrier gas of a selected type for each said chamber;

(c) means for inserting said selected carrier gas into each said flow path of each said chamber;

(d) means for splitting a sample gas and flowing said sample gas splits into each of said chambers;

(e) two electrodes spaced apart and located to respond to current flow resulting in sparks within each said chamber across said gas flow path and wherein the duration of said sparks minimizes electrode erosion and permits observation of phenomena occurring at and between said sparks and remote from said electrode location;

(f) means for measuring electrical currents resulting from ions which are produced by said sparks or by metastable species within said carrier gases interacting with said sample gas splits within each of said chambers; and

(g) computing means for processing said measured electrical currents to identify selected compounds contained within said sample gas.

98. The apparatus of claim 97 wherein said means for measuring said electrical currents comprises, within each detector chamber, a collector and a bias electrode cooperating with an electrometer.

99. The apparatus of claim 97 wherein said means for flowing said sample gas splits into each of said detector chambers comprises an injection tube entering each chamber through a fitting on said second end of said chamber.

100. The apparatus of claim 97 wherein said computing means for processing said

measured electrical currents to identify selected compounds contained within said sample gas further comprises a predetermined relationship between said measured electrical currents and the types of compounds yielding said measured electrical currents.

101. The apparatus of claim 97 wherein the major constituent of said carrier gases is helium.

102. The apparatus of claim 97 wherein minor constituents of said carrier gases comprise rare gases.

103. The apparatus of claim 97 wherein the resonance energies of the minor constituents of said carrier gases are different.

104. The apparatus of claim 103 wherein the resonance energy of at least one constituent of at least one said carrier gas is greater than the ionization energy of each of said measured compound within said sample gas.

105. The apparatus of claim 97 further comprising means for recording said identified compounds.

106. A method for analyzing a sample gas comprising the steps of:

(a) forming first and second carrier gases each comprising a mixture of an inert gas and different dopant gases;

(b) flowing a current through said carrier gases;

(c) energizing at least one component of said carrier gases to an excited state as a result of exposure to said current flow;

(d) mixing a sample gas comprising one or more compounds with said energized carrier gases;

(e) forming charged particles of said sample gas as a result of ionizing radiation emitted in the decay of said excited component of said carrier gases interacting with one or more compounds contained in said sample gas;

(f) measuring the electrical currents resulting from the flow of said charged particles wherein said measurement step occurs in timed relationship to carrier gas flow; and

(g) selectively identifying one or more said compounds contained in said sample utilizing said current measurements.

107. A method for analyzing a sample gas comprising the steps of:

(a) forming first and second carrier gases each comprising a mixture of an inert gas and different dopant gases;

(b) providing a detector chamber for each of said carrier gases;

(c) flowing each of said carrier gases through said provided detector chamber for exposure to current flow therein;

(d) energizing, within each said provided detector chamber, at least one component of each of said carrier gases to an excited state as a result of exposure to said current flow;

(e) providing a sample gas comprising one or more compounds;

(f) splitting said sample gas into portions thereby forming sample gas splits for flowing into each said provided detector chamber;

(g) exposing said sample gas splits to said energized carrier gases within each said provided detector chamber;

(h) forming charged particles within each said provided detector chamber as a result of ionizing radiation emitted in the decay of said excited components of said carrier gases interacting with one or more compounds contained within said sample gas splits;

(i) measuring the electrical currents resulting from the flow of said charged particles within each said provided detector chamber thereby forming a set of electrical current measurements; and

(j) identifying one or more compounds within said sample gas by utilizing said set of electrical current measurements and a predetermined relationship between said measured current set of the identity of said compounds.

108. The method of claim 106 wherein said dopants are selected such that the resonance energy of each said dopant is different.

109. The method of claim 106 wherein said dopants are selected such that the resonance energy of at least one dopant is greater than the ionization energy of each said identified compounds within said sample gas.

110. A method for analyzing a sample gas comprising the steps of:

- (a) exposing a first gas in a closed spark chamber to DC current across the chamber;
- (b) energizing at least one component of said first gas to an excited state as a result of exposure to said DC current and permitting the excited gas to form ionizing radiation by decay;
- (c) exposing a sample gas in a sample chamber to ionizing radiation resulting from the decay of at least one component of said first gas;
- (d) forming charged particles in said sample chamber as a result of exposure to said ionizing radiation;
- (e) measuring said charged particles wherein said measurement occurs in timed relationship to charged particle formation; and
- (f) selectively determining concentrations of compounds contained in said sample gas by utilizing said measurements.

111. The method of claim 110 wherein said first gas contained in said closed spark chamber is circulated by convective gas flow resulting from the heating of said first gas in the path of said DC current.

112. The method of claim 111 wherein said ionizing radiation is directed from said spark chamber into said sample chamber through a membrane window with minimal absorption of said ionizing radiation by said membrane window.

113. The method of claim 112 wherein pressure within said source chamber is balanced with pressure within said sample chamber.

114. The method of claim 113 wherein the energy of said ionizing radiation is below

the ionization potential of the major constituents of air.

115. The method of claim 114 wherein said first gas comprises krypton and said sample gas comprises air.

116. The method of claim 115 wherein the DC current is pulsed.

117. A gas sampling apparatus comprising:

- (a) a closed source chamber filled with a source gas;
- (b) a sample chamber with an inlet port through which sample gas flows into the sample chamber and an outlet port through which sample gas flows out of the sample chamber;
- (c) two electrodes spaced apart and protruding into said source chamber to define a spark gap across which short, repeated, high voltage pulsed DC current flows thereby raising at least one component of said source gas to an excited state;
- (d) a membrane window separating said source chamber and said sample chamber through which ionizing radiation, resulting from the decay of at least one said excited component of said source gas, passes from said source chamber to said sample chamber;
- (e) means of detecting charged particles formed in said sample gas resulting from the exposure of said sample gas to said ionizing radiation generated in said source chamber and passed through said membrane window into said sample chamber;
- (f) means for controlling the timing of said pulsed DC current and said charged particle detection; and
- (g) means for converting said detected charged particles to corresponding measures of concentrations of compounds within said sample gas.

118. The apparatus of claim 117 wherein said source gas is circulated within said closed source chamber by convective gas flow resulting from the heating of said source gas in the path of said pulsed DC current across said spark gap.

119. The apparatus of claim 118 wherein said means for measuring said charged

particles formed in said sample gas comprises a first electrode within said sample chamber maintained at a selected potential with respect to a second electrode within said sample chamber at ground potential.

120. The apparatus of claim 119 wherein said source gas comprises krypton.

121. The apparatus of claim 120 wherein said means for controlling said pulsed DC current and said charged particle collection comprises a clock which outputs timed pulses at predetermined and sequential intervals.

122. The apparatus of claim 121 wherein said means for detecting charged particles further comprises a charge collecting circuit which cooperates with said first electrode within said sample chamber and wherein the magnitude of the current induced within said charge collecting circuit is proportional to the concentration of the component of the sample gas providing said charged particles.

123. The apparatus of claim 122 further comprising a recorder cooperating with said charge collection circuit wherein said recorder is calibrated to convert said measured current magnitude to equivalent concentration of said component of the sample gas from which said particles are generated.

124. The apparatus of claim 119 wherein said window membrane is formed of magnesium fluoride or lithium fluoride.

125. The apparatus of claim 119 wherein said sample chamber and said source chamber are pressure balanced.

126. A method for selectively analyzing a sample of air for impurities comprising the steps of:

(a) exposing a source gas comprising krypton in a closed spark chamber to DC

- (a) exposing a source gas comprising krypton in a closed spark chamber to DC current;
- (b) energizing said krypton to an excited metastable state as a result of exposure to said current;
- (c) exposing said sample of air to ionizing radiation formed by the decay of said metastable krypton within said closed spark chamber where said ionizing radiation passes from said closed spark chamber into an adjacent sample chamber through a membrane window;
- (d) forming charged particles within said sample chamber by the selective ionization of impurities within said air sample while precluding the ionization of major constituents of air; and
- (e) determining concentrations of said impurities based upon measured magnitudes of said charged particles.

127. The method of claim 126 wherein said source gas contained in said closed spark chamber is circulated by convective gas flow resulting from the heating of said source gas by said DC current and the subsequent cooling of said gas convectively conveyed to locations within said closed spark chamber remote from said DC current.

128. The method of claim 127 including the step of directing ionizing radiation from said spark chamber into said sample chamber through a lithium fluoride or magnesium fluoride window with minimal attenuation.

129. The method of claim 127 wherein the air constituents of oxygen, nitrogen, water vapour and carbon dioxide are not energized and not detected and impurities with ionization potentials below 10.64 eV are energized and are observed.

130. The method of claim 74 wherein the sample component source is a gas chromatographic column.

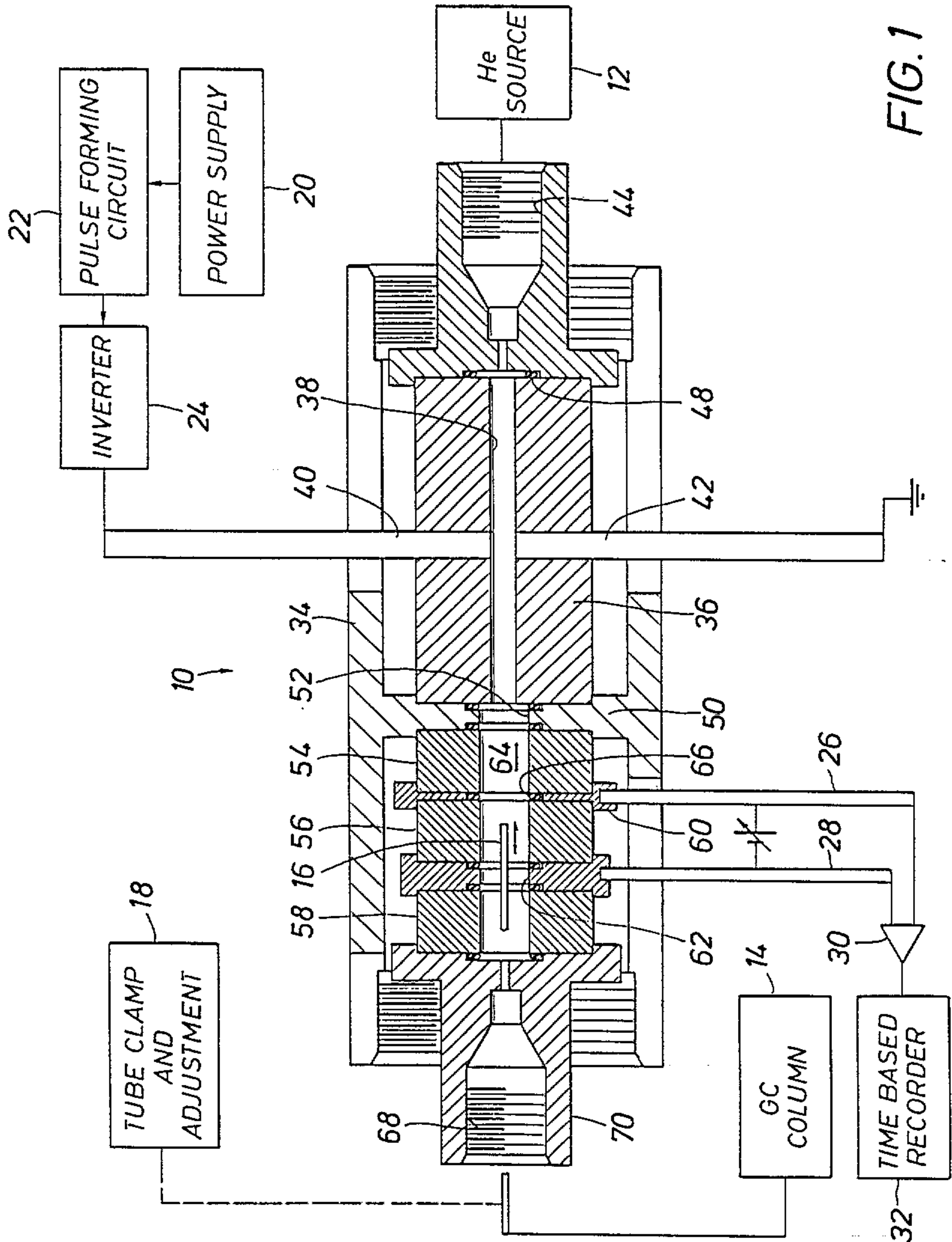
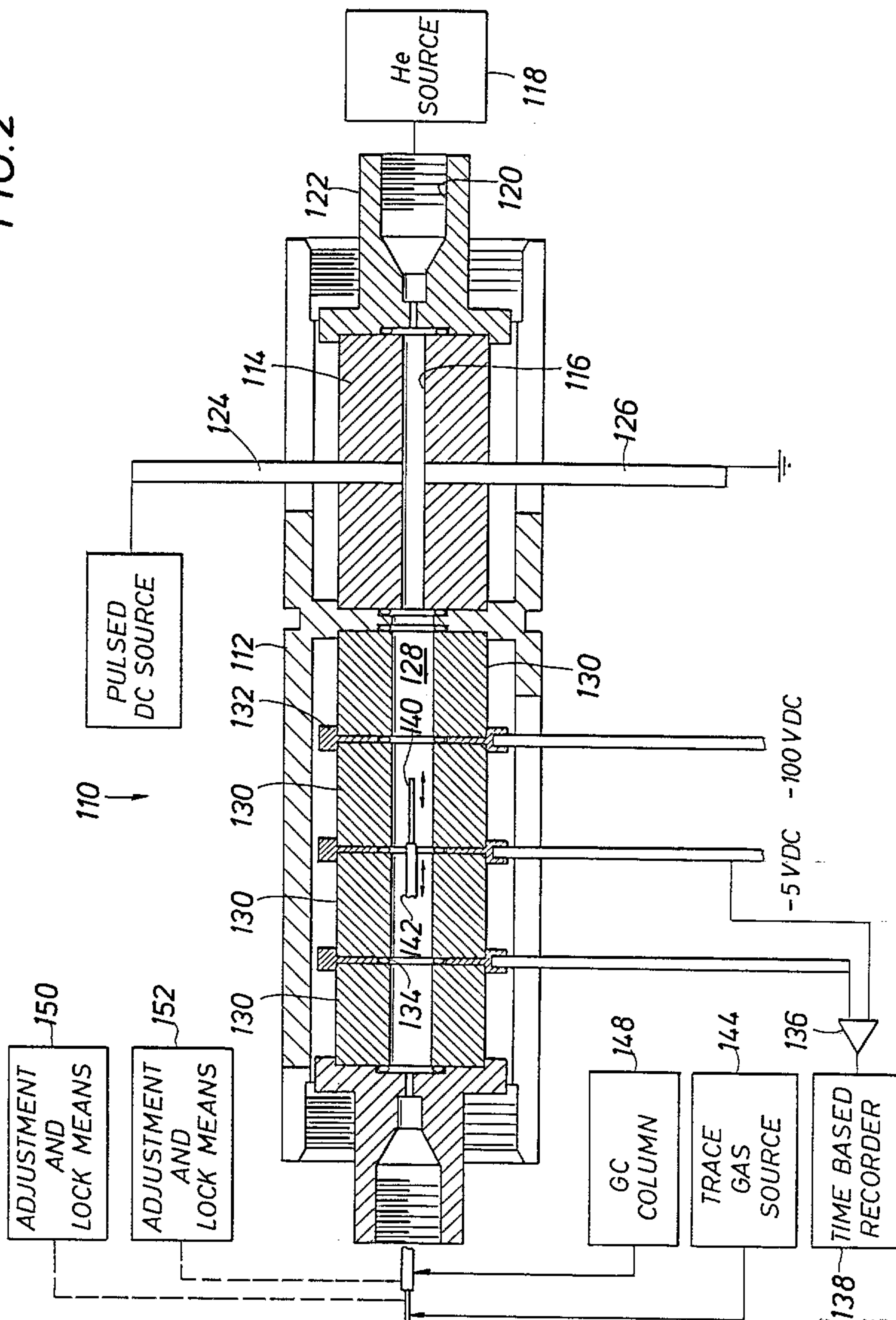
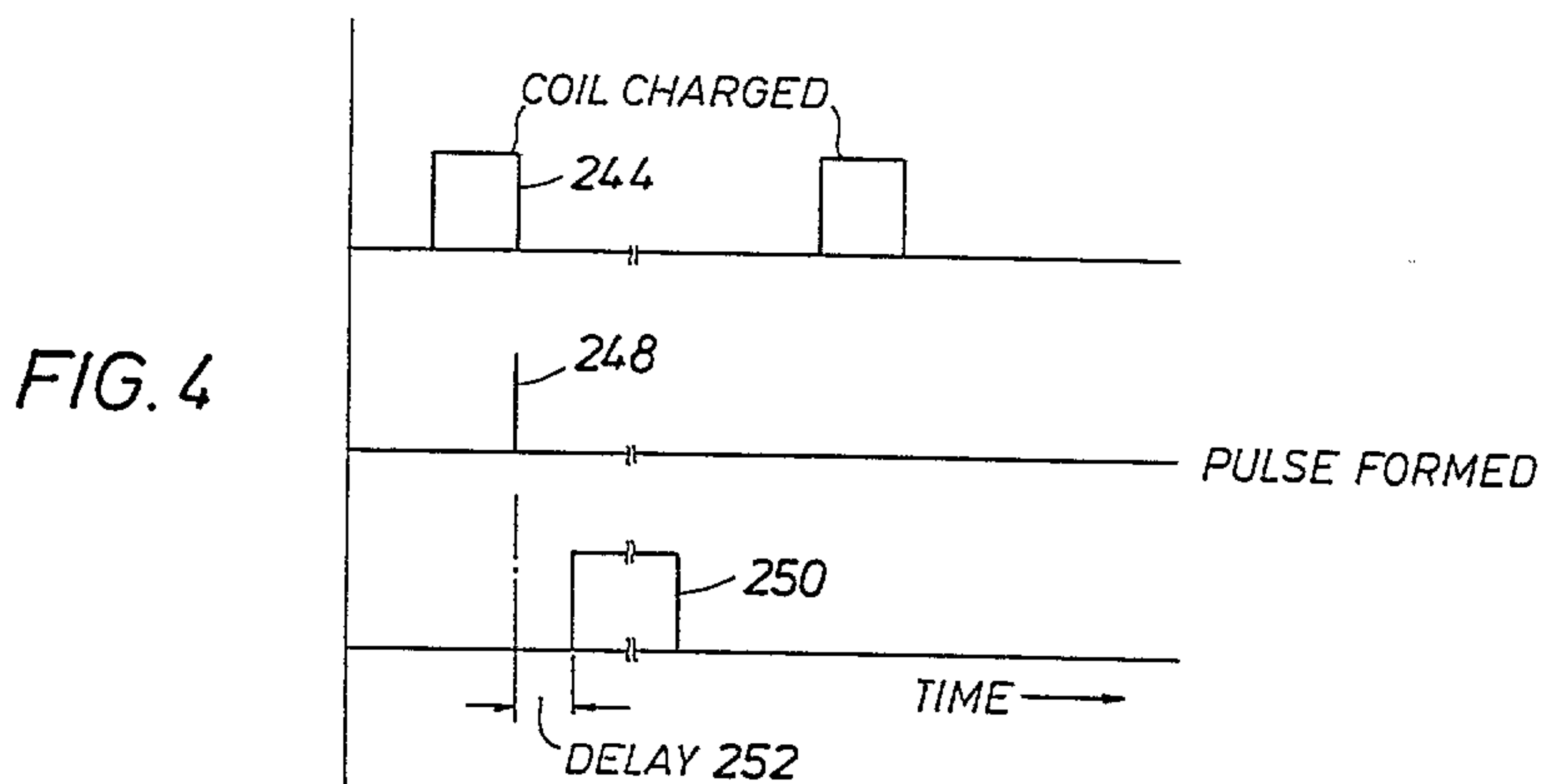
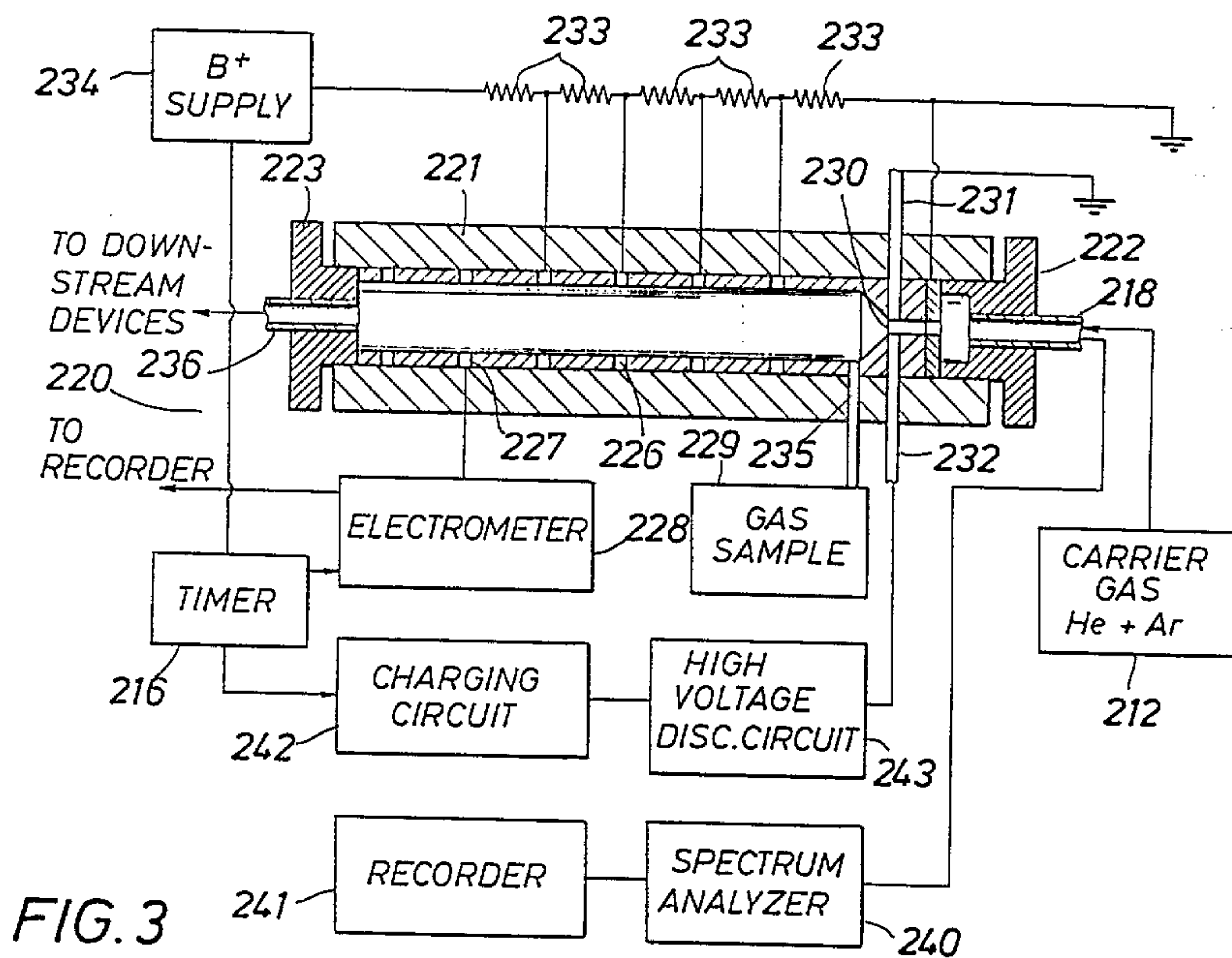


FIG. 1

FIG. 2





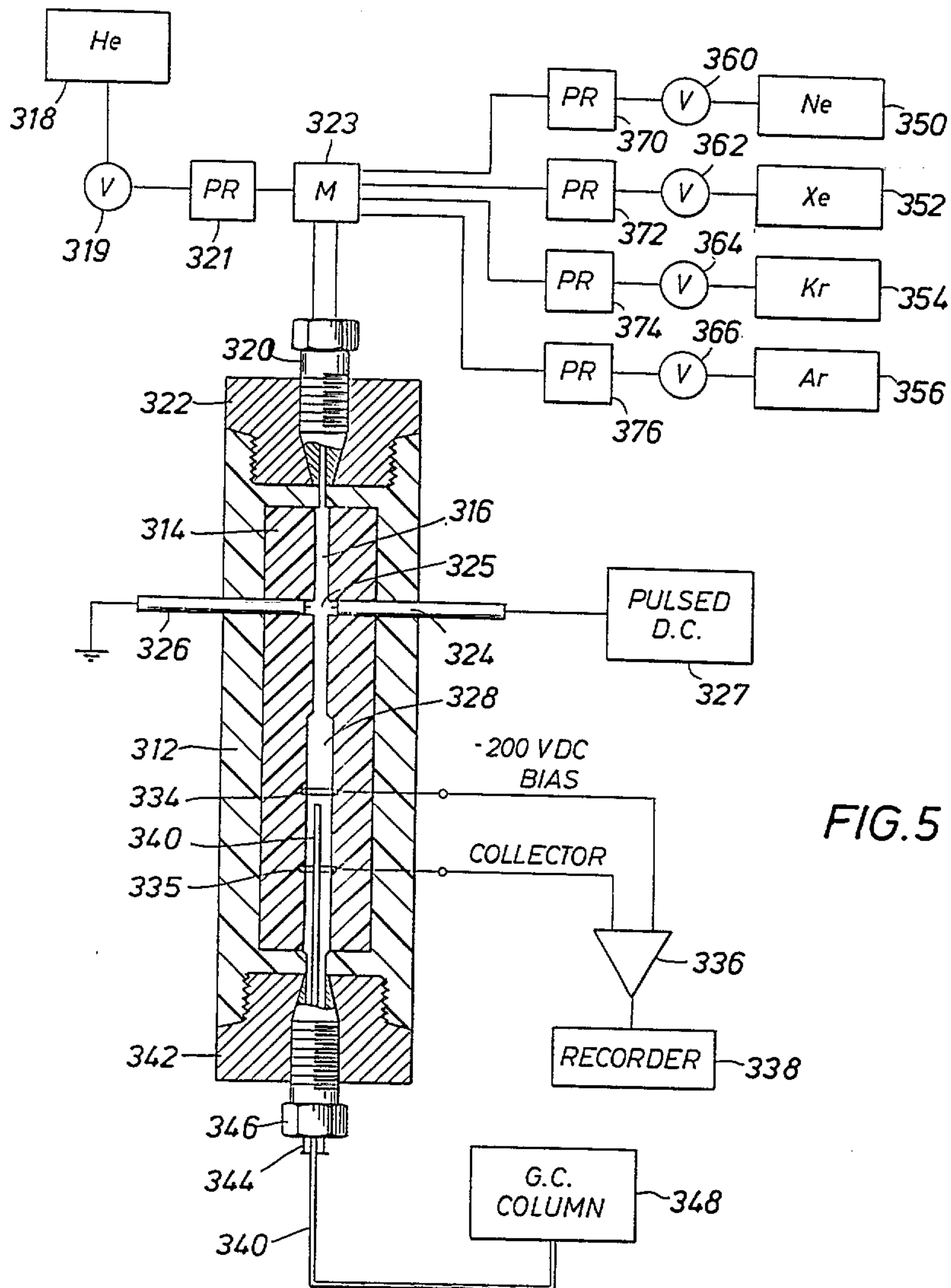


FIG. 5

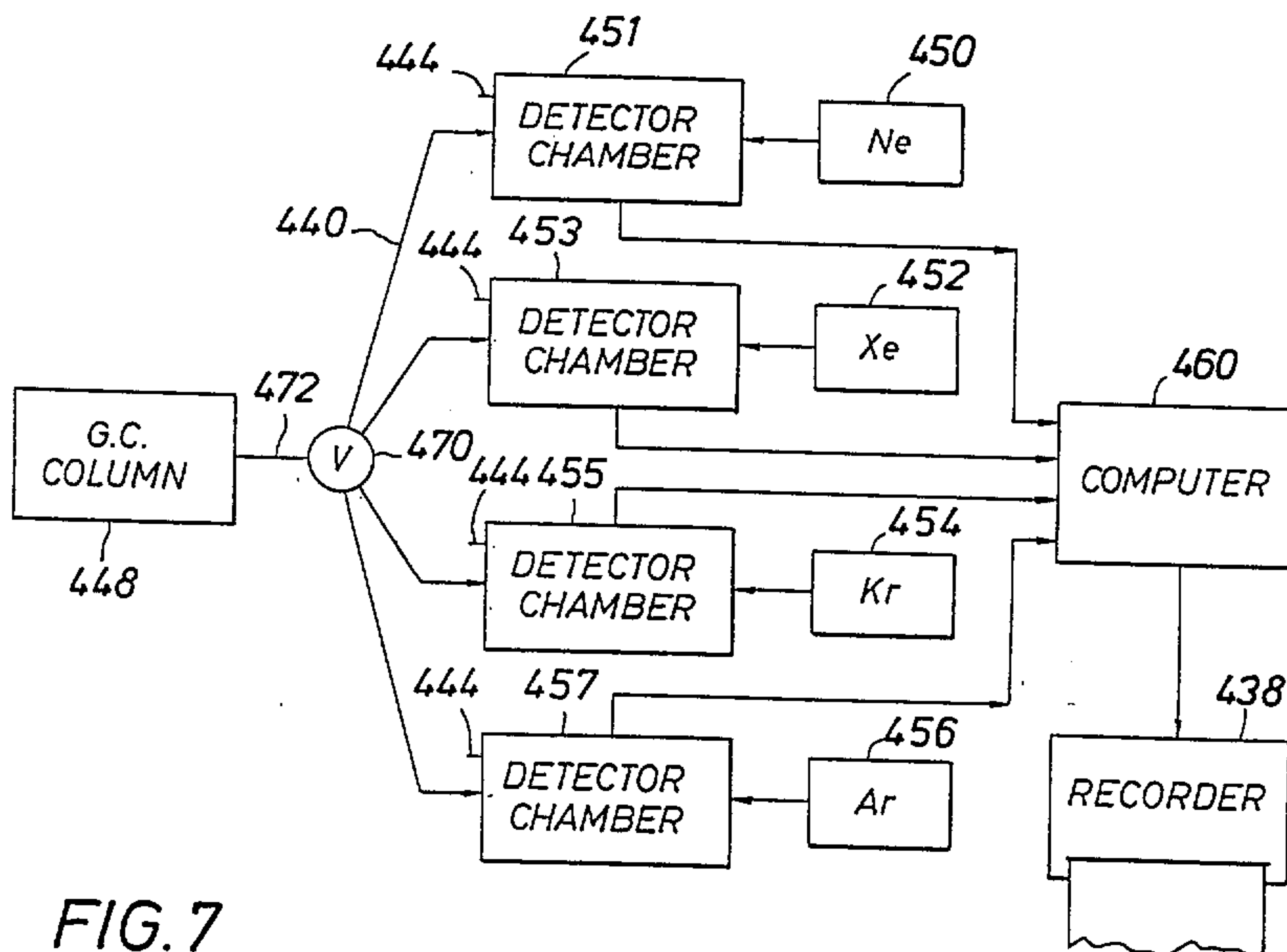
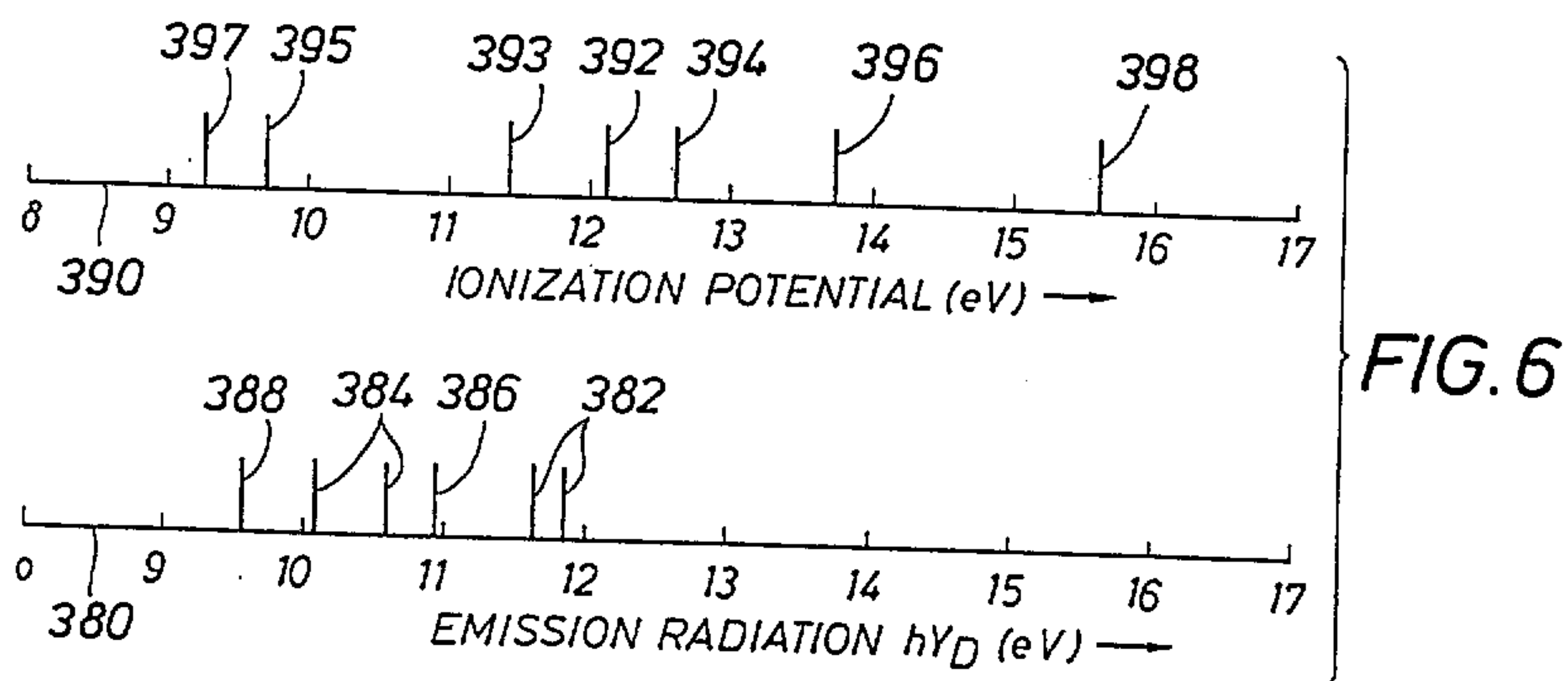


FIG. 7

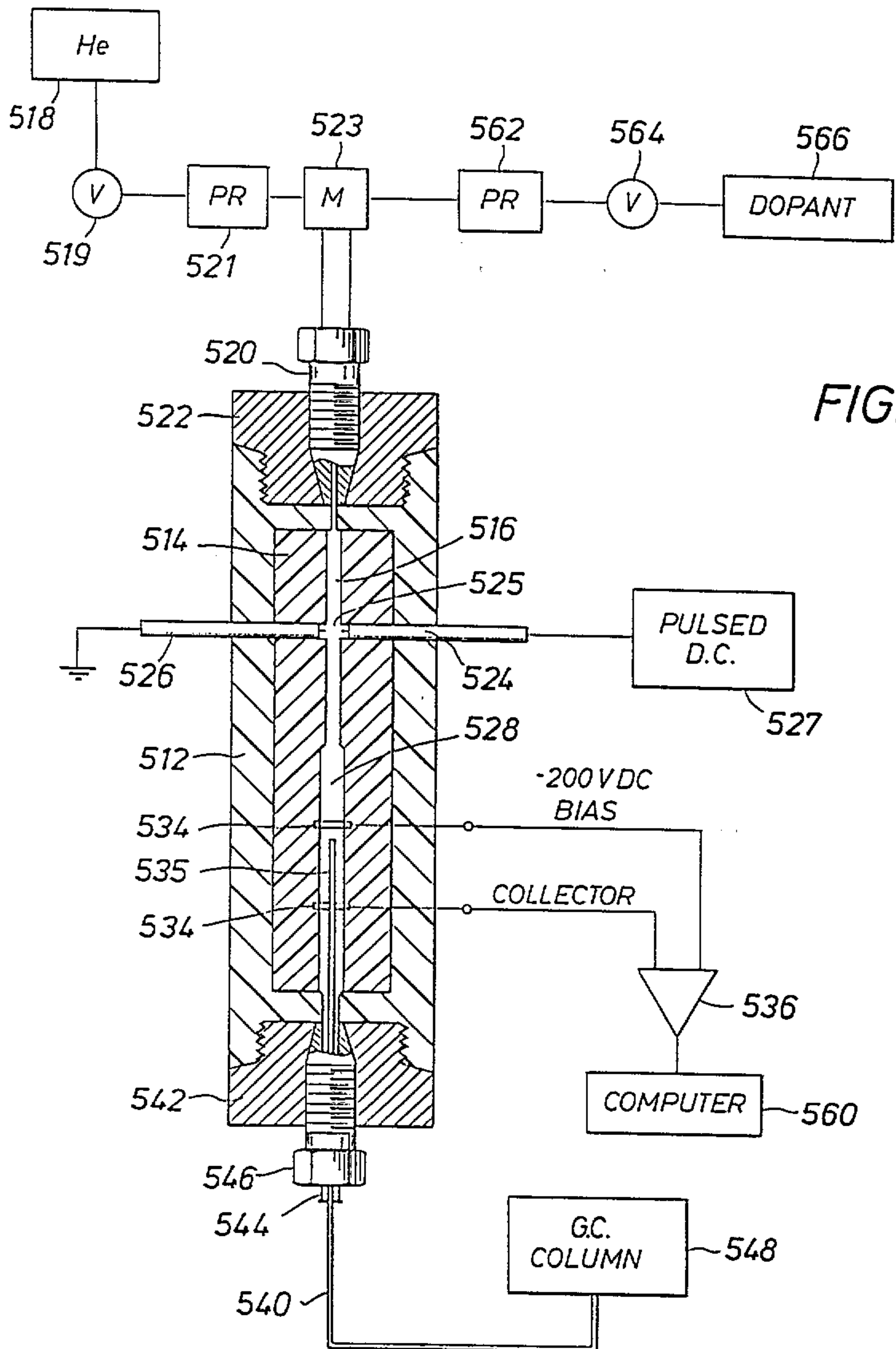


Figure 1 is a graph showing the relationship between the relative retention times of the first and second peaks (R_{Kr} vs R_{Ar}) for three compounds: CH_3CNO , PENTENE, and $CH_3H_7NO_2$. The y-axis (R_{Kr}) ranges from 0 to 60, and the x-axis (R_{Ar}) ranges from 0 to 90. Data points are marked with open circles and labeled with numbers 570, 572, 574, 582, and 584.

Compound	Label	R_{Ar} (approx)	R_{Kr} (approx)
CH_3CNO	570	78	42
	572	82	37
PENTENE	574	78	1
	582	0	5
$CH_3H_7NO_2$	584	10	0

FIG. 9B

60
50
40
30
20
10
0

R_{Kr} ↑

15 30 45 60 75 90

R_{Ar} →

582

2-METHYL-1-PENTENE

592

PENTENE

590

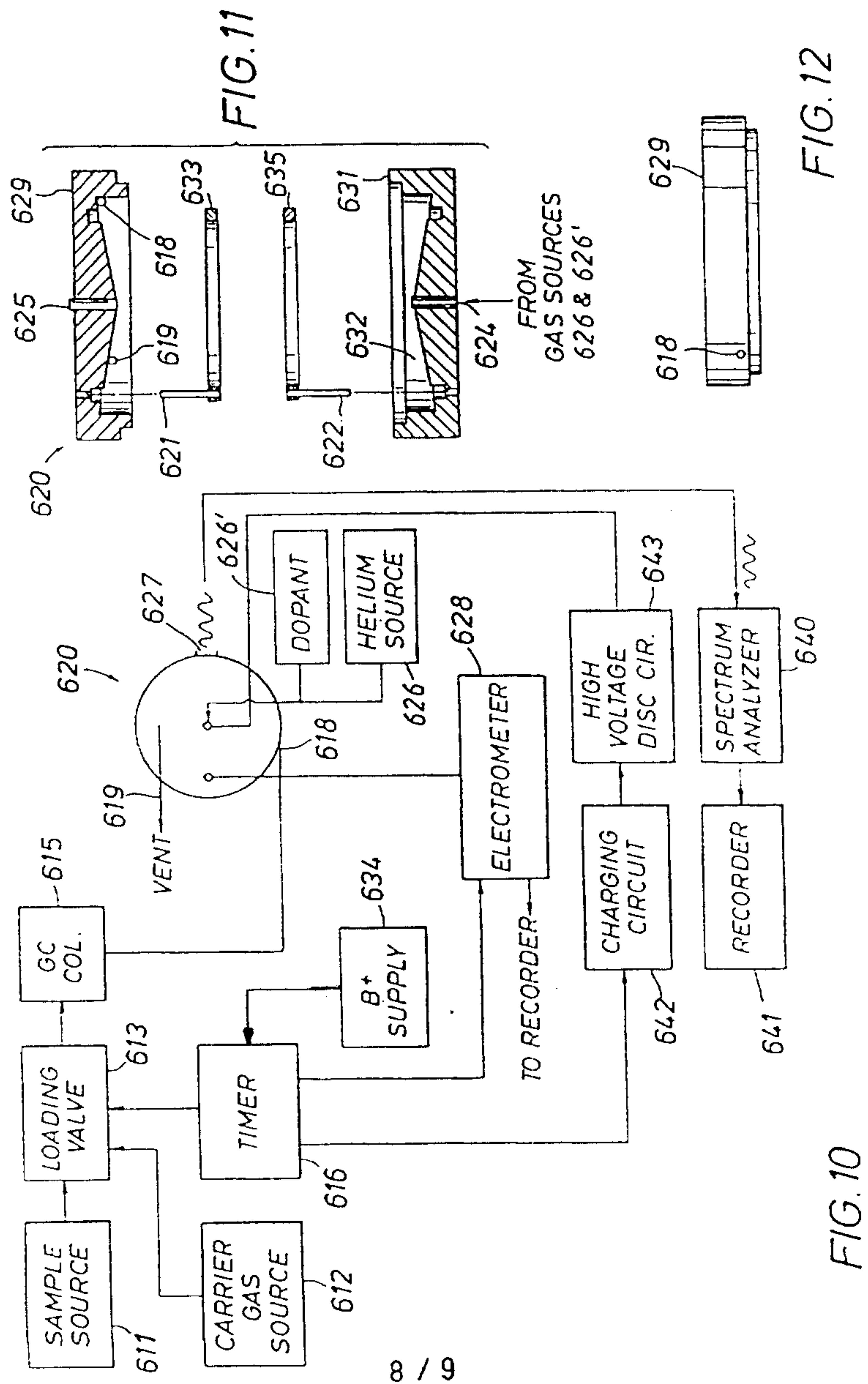
584

R^*

595

596

586



8 / 9

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PATENT AGENTS

FIG. 13

