Dec. 6, 1966 R. M. SCHIFF 3,290,501

APPARATUS FOR THE DETECTION OF RADIOACTIVE ISOTOPES ATTACHED TO MATERIAL OF GAS-LIQUID CHROMATOGRAPHY SYSTEMS

Filed Aug. 17, 1962 2 Sheets-Sheet 1

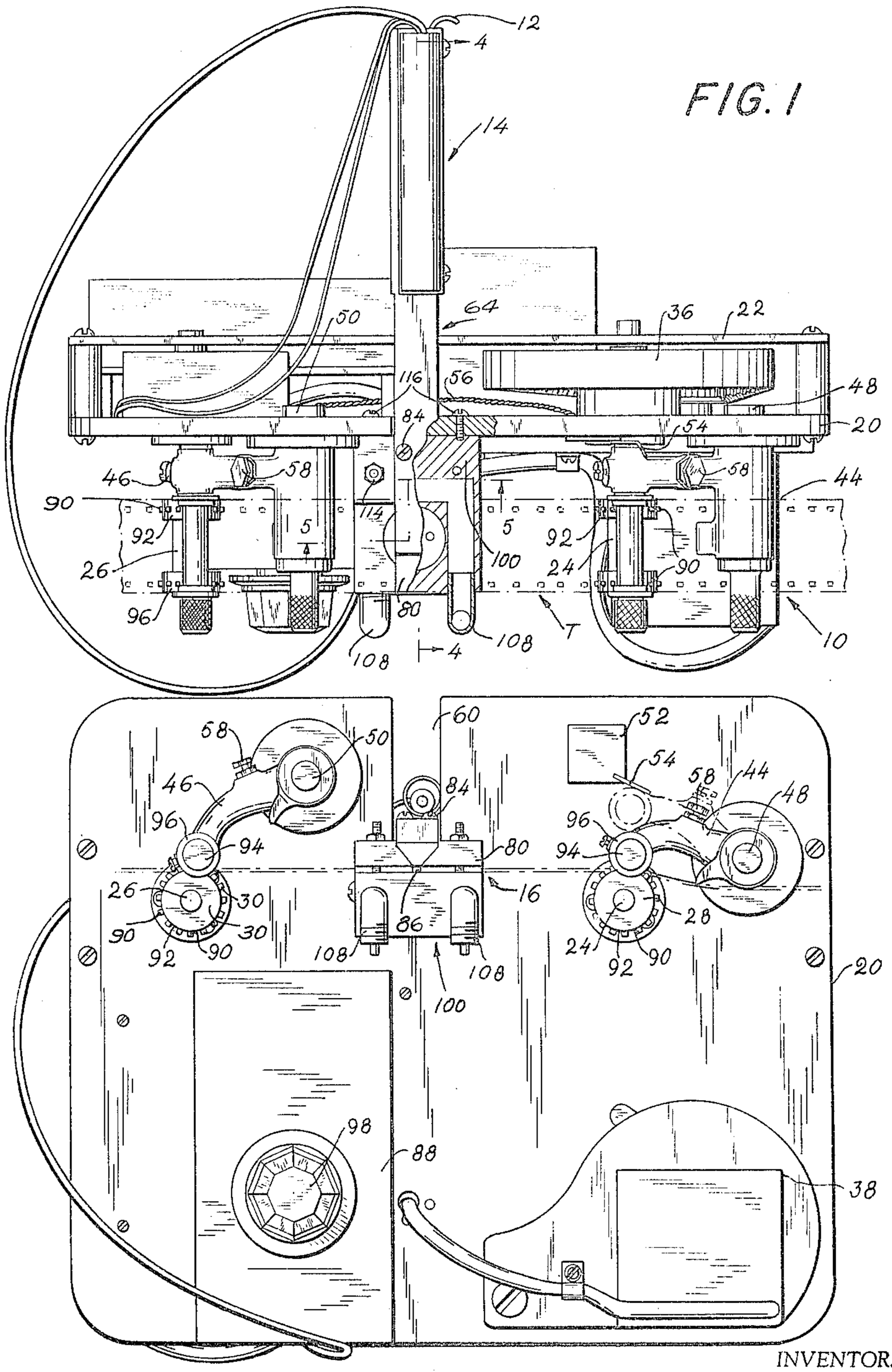


FIG. 1

FIG. 2

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FIG. 3

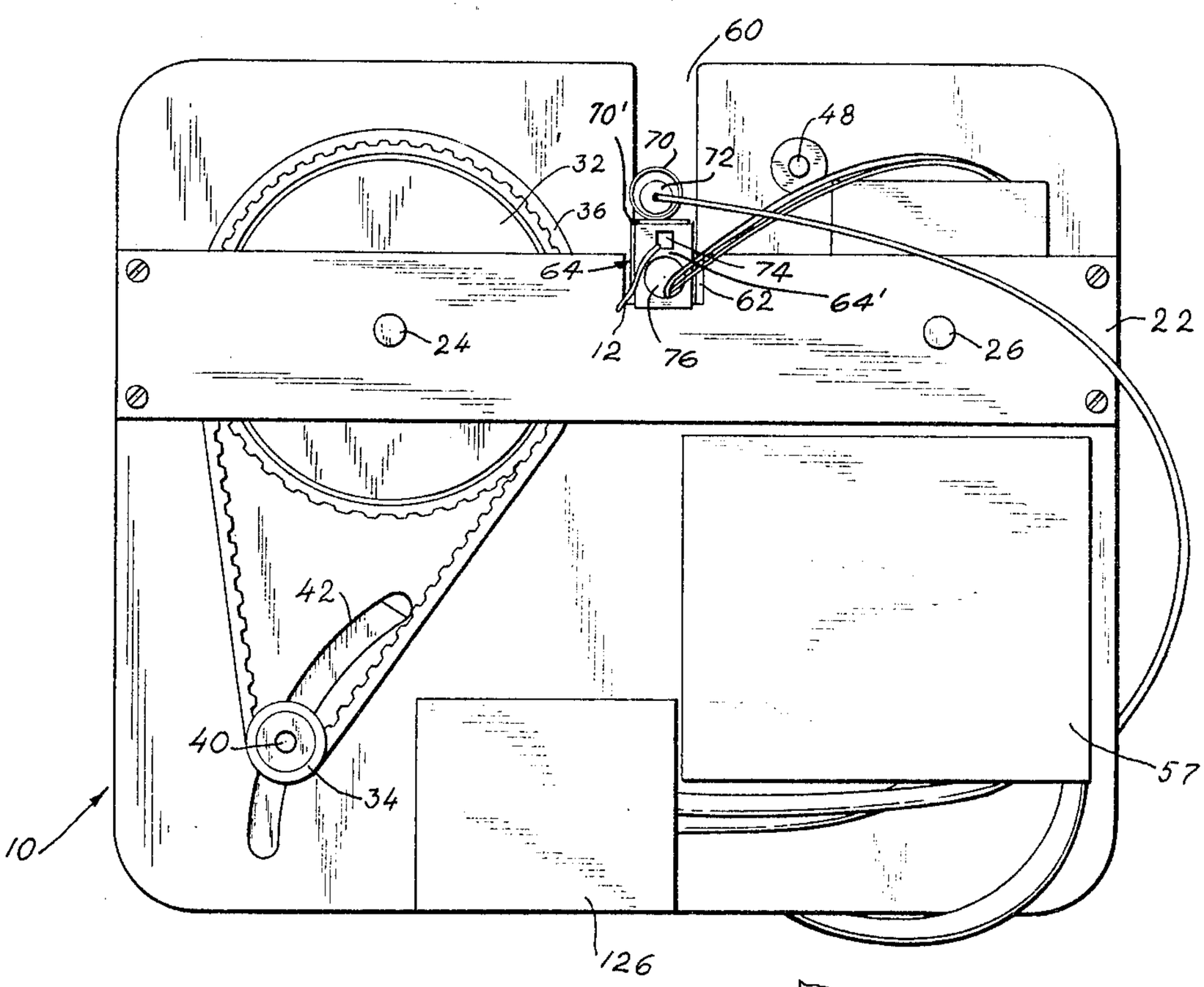


FIG. 4

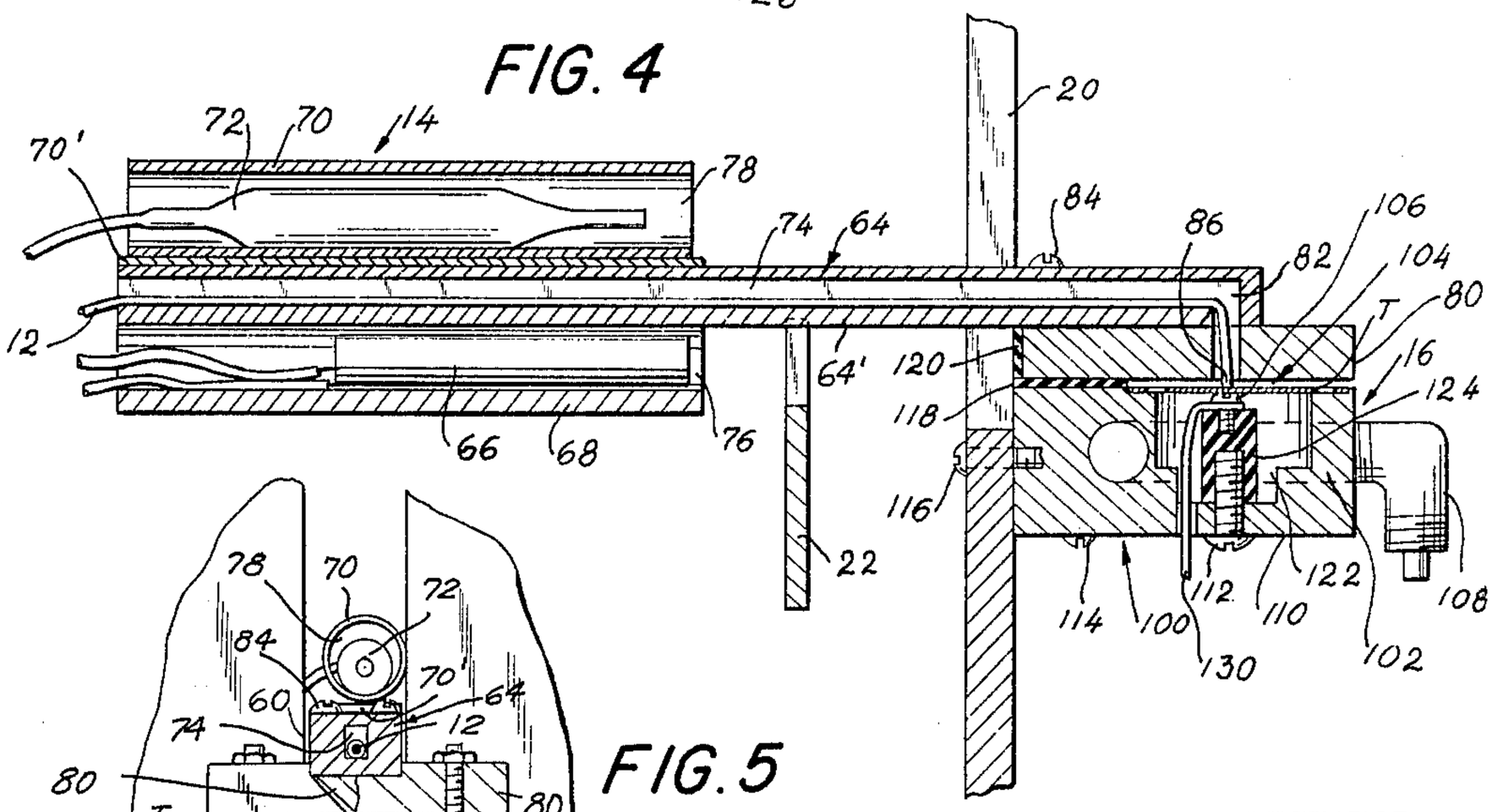


FIG. 5

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APPARATUS FOR THE DETECTION OF RADIOACTIVE ISOTOPES ATTACHED TO MATERIAL OF GAS-LIQUID CHROMATOGRAPHY SYSTEMS

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21 Claims. (Cl. 250—106)

This invention relates to novel and improved methods, apparatus and products for the detection of certain beta and gamma emitting isotopes when attached to the material of gas-liquid chromatography systems.

An isotope is any of two or more forms of an element having the same or very closely related properties and the same atomic number but different atomic weights or mass numbers. A radioactive isotope is generally that isotope of an element which gives off or is capable of giving off radiant energy in the form of particles or rays, as alpha, beta, and gamma rays. Within the context of the present invention, a radioactive isotope is intended to include solely any beta or gamma emitting isotope of an element having an energy level more active or higher than the energy level of tritium, and hereafter when mention is made of a radioactive isotope or radioactive isotopes, the afore-defined radioactive isotopes are intended.

As used hereinafter, effluent is intended to mean an inert gas stream, which stream may be argon, plus the particulate matter which leaves or comes off the column of a gas-liquid chromatographic apparatus. The particulate matter may include the radioactive isotope or isotopes or have the radioactive isotope coupled thereto.

More particularly, the present invention relates to novel apparatus, methods and products for the continuous collection, detection and/or storing of information providing an indication of the particular particulate matter to which the radioactive isotope is attached.

While the present invention is primarily intended for use with matter which is passed through gas-liquid chromatographic devices, such as for studies of intermediary metabolisms of biological systems and synthesis problems, it will be apparent to those skilled in the art that various other uses are possible, such as counting techniques.

A gas-liquid chromatographic system for analyzing matter is generally similar to a fractionating system in which the lighter products come off or leave the column first and the heavier products following and leaving the column subsequently in accordance with their relative weights. In the chromatographic system, samples are broken down or separated into their various derivatives or components.

The present invention proposes to provide a material which is responsive to radioactive isotopes. The present invention proposes to collect, detect and/or store the radioactive isotope when used as a tag. This tag is either placed into matter under study or already forms part of the matter under study. The matter under study within the context of the present invention is that material which passes through the column of a gas-liquid chromatographic system. An example of the radioactive isotope which is to be used as a tag is the C^{14} radioactive isotope.

It is also to be understood that the tag is the isotopic form of the element which has been artificially or chemically introduced into a compound or the matter under study by well-known conventional methods to replace the non-isotopic form so that chemical change, migration, or transformation may be followed within the compound after the compound is broken down into its various components or constituents by such methods as gas-liquid chromatography.

When the tag is first introduced into the compound,

the tag either adds itself to the compound or replaces the natural non-isotopic form of the element. For example, tritium would replace the non-isotopic form of hydrogen and the compound water would be changed from H_2O to $H_2{}^3O$. The tag merely acts as a guide so that it can be followed with the compound.

If it is assumed that the compound or material under study contains the constituents A, B, C, D and E—the tag or radioactive isotope may be one of the aforesaid constituents, or the tag may be introduced into the compound and attach itself to one or more of the constituents and replace its non-isotopic form. Where the tag forms one or more of the constituents A, B, C, D, E, the tag is detected, collected or stored in accordance with the present invention and based upon its time of exiting from the column of the gas-liquid chromatographic apparatus, the radioactive constituent or constituents is ascertained. Where the tag is introduced into the compound, it will attach itself to one or more of the constituents A, B, C, D and E, and knowing the quantity of the tag introduced, the quantity in addition to the presence of the tag attached to one or more of the constituents can be continuously and individually ascertained.

Present day radioactive isotope detection systems are not adapted for continuous operation. It has been found that the present available apparatus and detection systems are not able to collect and/or record low radioactivity energy levels, i.e. C^{14}, T^3.

An example of a well known radioactive isotope detection system which is not continuous is one which uses a "Popjak" detector. The Popjak detector may be characterized as a liquid scintillation detector particularly designed to recirculate the effluent of a gas-liquid chromatographic column in a liquid scintillating medium forming with the use of appropriate circuitry an indication of cumulative radioactive material. In this system, it is important to note and appreciate that the scintillating medium used is a liquid phosphor. The liquid phosphor which is used is diphenoloxizol benzine (PPO).

In another well known present day type of gas-liquid chromatographic detection system, use is made of the well-known "Lovelock" or argon detector. With the Lovelock detector, the radioactive isotope cannot be used as the tag as it cannot be collected or detected. When the Lovelock detector is used, the sample is introduced into the gas-liquid column in solution. The solution is heated, vaporized and subsequently drawn through a column via a carrier, generally argon gas. The particular type of technique which is used is the "packed-column" type although other techniques are also available. The column is packed with a material which is called a Chromasorb (obtainable from Johns-Manville Co.) and is similar to a fine crushed pumice-like substance. While argon gas is generally used as the carrier gas to convey the sample through the column, any inert gas may be used.

The Lovelock or argon detector depends upon two actions. One is the excitation of argon atoms to a metastable state by electron bombardment, and the other is the ionization of vapor molecules as a result of the transfer of energy produced by the collision with the metastable argon atoms. This detector requires a radioactive source, and because it operates on the principle of ionization of the vapor molecules, it is incapable of detecting the radioactive isotope or tag in accordance with the present invention. Also, it imparts its characteristics to the material to be detected.

The Lovelock detector, therefore, is not capable of detecting the radioactive isotopes; only the other or non-radoactive isotopes are detected by the Lovelock detector. Present day methods and appartus as exemplified by the

Lovelock detector may be considered to be "radioactive detectors" or "ionization detectors."

A "radioactive detector" or "ionization detector" is a detector capable of detecting non-radioactive derivatives which come off the column of the gas-liquid chromatographic apparatus and which uses radioactive materials themselves in the detection process and as elements forming part of the detector apparatus.

Accordingly, it is a primary object of the present invention to provide a detector capable of detecting radioactive materials, particularly the radioactive isotope or isotopes, coming off the column of gas-liquid chromatographic apparatus without having the detector system impart any of its own characteristics to the material to be detected.

Prior to the present invention with the use of the conventional "radioactive detectors" it was not possible to detect the quantity of, and including the mere presence of the radioactive isotope. The prior art devices use a "radioactive detector" to detect non-radioactive derivatives, and the present invention proposes to provide methods and apparatus for the detection of radioactive derivatives not heretofore detectable by the present day "radioactive detectors."

The present invention may be used separately or together in parallel with the aforementioned prior art detectors. The detector of the present invention is a nuclear device which permits and provides for the determination of the radioactive isotope concentration of the various components or constituents introduced into the column of the gas-liquid chromatographic apparatus.

Since the present day detectors, as exemplified by the Lovelock detector, ionize or impart radioactivity to the material as it comes off the column, a conventional T-connection is provided to draw-off a portion of the material coming off the column. In a practical embodiment of the present invention, approximately ten percent (10%) of the material coming off the column is usually supplied to the detector and collector system of the present invention. While ten percent (10%) of the material is to be supplied, this is not limiting, but preferable. If the level of activity of the sample is low, then more than ten percent (10%) of the material coming off the column should be supplied to the detection system of this invention. The quantity of material coming off the column to be used depends upon the level of activity of the sample and is not a limitation of the invention. The remaining ninety percent (90%) may go off from the column without any detection or for other purposes or a portion, generally ten percent (10%), may also be supplied to the Lovelock detector to detect the non-radioactive components or derivatives. The apparatus of the present invention is a radioactive isotope detector and collector which will continuously detect the presence of and collect the quantity of and store the radioactive isotope or isotopes present in the inert gas stream coming off the column.

The Lovelock detector or other equivalent prior art ionization detector which detects the presence of the various derivatives is incapable of providing a separate and distinct indication between a tag and an ionized particle; the Lovelock detector by virtue of its operation places radioactive by-products into the inert gas stream as it vents or comes out of the chamber. Collection of these radioactive products with present day apparatus is impractical as these radioactive products increase the radioactive background, i.e. due to the other constituents which are not part of the material of fractionation. The Lovelock detector will detect the presence and quantity of the non-radioactive isotopes or components present in the inert gas stream, and therefore may be considered to be an ion detector as distinguished from the present invention which will detect the presence and quantity of the radioactive isotopes present in the inert gas stream.

The apparatus of the present invention may be used separately or in parallel with the Lovelock detector so as to detect both the radioactive isotopes and to determine the ion concentrations.

The various components of the gas effluent coming off the column goes through the T-connection and from one leg thereof is applied to the apparatus of the present invention in the vapor state. From a physical point of view, the state of the inert gas stream is that of a vapor. The vapor concentration is directly related to the ion concentration. The temperature of the vapor or effluent is approximately 225° C., and if the effluent were vented to air, the vapor would condense, rise and have the outward appearance of cigarette smoke.

It is therefore another object of the invention to provide methods of and apparatus for collecting and then detecting accurately and reliably both the position and quantity of the radioactive isotope with respect to the chromalagram.

A further object of the invention is to determine the radioactive isotope concentration of an effluent.

Another object of the invention is to provide a medium onto which the radioactive isotope may be trapped.

Yet another object of the invention is to provide a medium for the continuous recordal of the radioactive isotope concentration in each of the fractions.

Still another object of the present invention is to provide a solid medium for the storing of the radioactive isotope.

In order to accomplish the foregoing objects, the present invention proposes to take the vapor carried by the inert gas stream, which is the effluent, and supply it to an apparatus which will detect and/or collect and/or store the radioactive isotope and which will not contaminate the effluent with any radioactivity during and while detecting, collecting or storing the radioactive isotope.

The inert gas stream is taken from the column of the gas-liquid chromatographic apparatus and supplied to a collection and detection apparatus according to the present invention. The collection and detection apparatus generally includes means to maintain the inert gas stream heated to prevent condensation and thereby loss of efficiency. The apparatus also includes means to carry a moving tape prepared in accordance with this invention as described further hereinafter and means to precipitate the radioactive isotope onto the tape whereby to provide an indication on the moving tape of the presence, quantity and position of the radioactive isotope in the inert gas stream.

In order to prevent buckling of the tape and assist in electrostatic precipitation of the radioactive isotope, the apparatus includes cooling means, such as means to recirculate cold water.

The means to carry the tape includes a tape transport mechanism to move the tape past the output taken from the column in order to provide for the continuous recordal of the amount, position and mere presence of the radioactive isotope in the effluent as the effluent exits from the column. The tape transport mechanism moves the tape past the output of the column at a predetermined rate or velocity to provide a time base for the tape so that the times of exiting of the radioactive isotope from the column can be ascertained.

The tape in accordance with the present invention is a "Mylar" tape coated with a mixture of anthracene and polyester, such as acrylic. While the coated tape is especially well adapted for use with beta emitters, as exemplified by carbon C^{14}, the tape is generally useful with all beta and gamma emitting isotopes.

The objects, advantages and nature of the invention will be more fully understood from the following description of the preferred embodiments of the invention, shown, by way of example, in the accompanying drawings, in which:

FIG. 1 is a plan view, partially in section, of the collection and detection apparatus;

FIG. 2 is a front elevational view of the apparatus shown in FIG. 1;

FIG. 3 is a rear elevational view of the apparatus shown in FIG. 1;

FIG. 4 is a sectional view taken on line 4—4 of FIG. 1 showing in detail the means to couple the output of the column of the gas-liquid chromatographic apparatus to the means to precipitate the radioactive isotope onto the moving tape; and,

FIG. 5 is a sectional view taken on line 5—5 of FIG. 1.

Referring now more particularly to the drawings which illustrate the small particle collection and detection apparatus and includes a tape transport mechanism **10** arranged to transport and support a moving tape T shown in phantom, a Teflon tube **12** to take the effluent off directly or through a T-connection from the packed column of a conventional gas-liquid chromatographic apparatus (not shown), a feeder assembly **14** to feed the effluent to the tape T and an anode assembly **16** for transferring the constituents of the particulate matter in the effluent including or coupled to radioactive isotope or isotopes from the effluent to the tape T shown in phantom. Tape T is generally similar to conventional edge-perforated 35 mm. film, although any commercially available tape prepared as set forth hereinafter may be used.

The tape transport mechanism **10** includes a front upright member **20** and a rear support member **22** spaced therefrom and fixed thereto by means of suitable connection members and spacers. Upright member **20** is preferably formed of aluminum or other suitable material having good thermal conductivity in order to dissipate heat rapidly from the feeder assembly **14**. The feeder assembly **14** is to be maintained at 225° C. to prevent condensation of particles in the inert gas stream, and to maintain a high efficiency. A pair of rotatable shafts **24**, **26** are suitably journaled for rotation between members **20** and **22** and suitably supported thereby. Shafts **24** and **26** are positioned on opposite sides of the feeder assembly **14** and anode assembly **16** and carry a pair of sprockets **28** and **30**, respectively. Sprockets **28** and **30** are fixed to shafts **24** and **26** for rotation therewith, with sprocket **28** being a drive sprocket and sprocket **30** being a driven sprocket. Also coupled to shaft **24** and fixed for rotation therewith is a conventional gear belt driven toothed gear belt pulley **32**, see FIGS. 1 and 3, arranged to be driven by a conventional belt drive toothed gear belt pulley **34** by means of a conventional coupling belt **36**, such as a "Gearbelt" (a registered trademark) belt. Coupled to the front of the front upright member **20** is a conventional drive motor **38** having its output shaft **40** extending through an adjustable gravity slot **42** and coupled to the belt drive gear belt pulley **34**. The motor **38** when energized is effective to rotate drive sprocket **28** but has no effect upon the driven sprocket **30**. The only connection between drive sprocket **28** and driven sprocket **30** is the tape T. The tape T is moved by the drive sprocket, and since it is suitably held to the driven sprocket, the movement of the tape T is effective to drive the driven sprocket **30**. The tape T is moved in a predetermined time relationship related to time of exiting of the effluent from the packed column.

Associated with each of sprockets **28** and **30** is a conventional L-pad **44** and **46**, respectively, which may be conventional spring loaded pad rollers and is supported by means of supports **48**, **50**, respectively, carried by the front upright member **20**. Supports **48** and **50** are fixed to the face of the front upright member **20** and extend therefrom. Each L-pad is arranged to pivot on its respective support into and out of engagement with its respective sprocket. Sprockets **28** and **30** may suitably be conventional 35 mm. film carrying sprockets and are provided with conventional peripheral teeth **90** adapted for engagement with the edge perforations of a conventional film, e.g. 35 mm. film. Teeth **90** project from drum surface **92** which is a substantially smooth outer cylindrical surface. Pads **44** and **46** are shown in full outline (FIG. 2) in engagement with the tape T and sprockets **28** and **30**, and the pads may be raised or pivoted on their respective supports to the position shown in phantom to facilitate removal from and placement of the tape T onto the sprockets.

In order to prevent motor **38** when operative from rotating sprocket **28** with its associated L-pad **44** in its raised position shown in phantom, a safety switch **52** which may suitably be a microswitch is provided. Microswitch **52** includes an arm **54** arranged to be engaged by the L-pad **44** to shut off the motor **38** when the L-pad **44** is in its aforesaid raised position as shown in phantom, electrical connecting wires **46** being provided to connect the microswitch **52** electrically with the motor **38** and a high voltage supply **57** to deenergize the motor **38** and the supply **57** in a conventional manner.

Adjusting screws **58** are provided on each of the L-pads **44**, **46** to adjust the tension of the L-pads **44**, **46** when in engagement with sprockets **28**, **30**, respectively, when tape T is positioned therebetween to provide sufficient pressure to prevent disengagement of the tape from and to move the tape upon rotation of sprocket **28**. Also, the tension on the tape T must not be so large as to damage the edge performations.

The tape T is prevented from falling off the sprockets by means of the L-pads. The L-pads permit sufficient clearance between the tape T and the sprockets **28**, **30** so that the portion of the tape between the edge perforations is free of any contact either with the L-pads or the sprockets. The speed of the tape or the driving velocity of the tape is maintained at a predetermined time relationship to the time of exiting of the effluent from the column and is desirably approximately one-half (½) inch per minute or 13 mm. per minute although any calibrated velocity may be used. The two sprockets are accurately and precisely centered with respect to each other so that all portions of the tape T lie in the same plane and are not warped or bent during transport and will not become disengaged during transport. L-pads **44** and **46** are each provided with a pair of substantially smooth freely rotatable members **94** having substantially smooth outer cylindrical surfaces **96** arranged to engage the portions of surfaces **92** outside of the peripheral teeth **90** when tape T is not being carried by the sprockets and arranged to engage the portion of tape T on the outer periphery thereof outside of the perforations and not between the perforations, thereby not interfering with the tape and the coating carried thereon. A suitable tape take-up device (not shown) may also be provided.

The front upright member **20** is provided with a U-shaped recess **60** which is in registry with a similar U-shaped recess **62** provided in the rear support member **22** and is arranged to receive the feeder assembly **14**. The feeder assembly **14**, see FIG. 4, includes an outer casing member **64** to enclose and protect the Teflon tube **12**, the casing member **64** being positioned within and supported by the U-shaped recesses **60** and **62** for positioning of the tube **12** above the tape T. A positioning and holding block **80** having an opening passageway **82** is either fixed to outer casing member **64** by means of screws **84** or may be formed integral with the casing member **64** to maintain tube **12** enclosed just above tape T with the exit portion **86** of the tube **12** just above the tape T and outside of block **80**. A cartridge heater **66** which is encased within a metallic casing member **68** is positioned next to the casing member **64** so that the heater **66** will maintain the effluent carried by the Teflon tube **12** heated so as to prevent condensation of the material in the gas stream coming off from the column of the gas-liquid chromatographic apparatus and thereby also prevent any loss of efficiency. Casing members **64** and **68** may suitably be formed as an integral unit with chambers **74** and **76** formed therein or separately as two individual casing members. On the top of casing member **64** there is provided another outer

casing member **70** arranged to enclose a thermostatic sensing element **72**. Positioned between casing members **64** and **70** is a plate **70'** so that the top wall portion of casing member **64** beneath and supporting casing member **70** will have the same thickness as the intermediate wall **64'** of casing member **64** positioned between tube **12** and the heater **66** so that thermodynamically the heater **66** and the thermostatic sensing element **72** are in the same heat exchange relationship with tube **12**. It is to be understood that casing members **64**, **68** and **70**, while shown as two separate casing members may be formed as three separate casing members **64**, **68**, and **70** or may be formed together with block **80** as a single integral casing member provided with three chambers **74**, **76** and **78**, so as to position the heater **66**, the thermostatic sensing element **72**, the block **80** and the Teflon tube **12** in heat-exchange relationship with each other, whereby to maintain a substantially constant temperature in the inert gas stream carried by the Teflon tube **12**. The integral casing members **64**, **68**, **70** and block **80** may suitably be formed of brass, and if individual casing members **64**, **68** and **70** and block **80** are used, these may also be suitably formed of brass.

The cartridge heater **66** is connected to a temperature calibration device **88** which is carried on the face of the front upright member **20**. The temperature calibration device **88** includes a conventional thermostat (not shown) and is coupled with the thermostat sensing element **72**. The thermostat (not shown) is responsive and variable in response to the thermostat sensing element **72** to increase or decrease the heating effect of the cartridge heater **66** to maintain the inert gas stream at a substantially constant temperature. The temperature calibration device **88** may be set for a predetermined temperature by means of temperature calibration knob **98** to preset the quantity of heat imparted to the Teflon tube **12**; the thermostat sensing element **72** since it is in heat-exchange relationship with tube **12** and cartridge heater **66** is effective to control the heating effect of the cartridge heater, and for this purpose the temperature calibration device **88** includes the conventional thermostat (not shown).

The thermostatic sensing element **72** is connected with the thermostat to render the cartridge heater operative or inoperative, as it is necessary to maintain the inert gas stream heated to prevent condensation as it passes through tube **12** for exiting at **86** and loss of efficiency in the operation of recording the position and quantity of the radioactive isotope or isotopes with respect to the chromalagram.

The anode assembly **16** includes a positioning block formed by the holding block **80** and a collection block **100** provided with cooling water recirculation passageways indicated generally by **102**, and an anode structure **104** which includes an anode **106**, shown as a screw, in contact with the underside of tape T, aligned with opening passageway **82**, and in registry with the exit portion **86** of tube **12** which exit portion is positioned on top of but not in contact with tape T.

Coupling orifices **108** are provided to connect recirculating cooling water to the anode assembly **16** for recirculation through passageways **102**. The cooling water is effective to prevent buckling of the tape T and assists in the precipitation of the radioactive isotope.

The collection block **100** has a lower portion **110** which is coupled to the holding block **80** by suitable coupling means such as screws **114**. The holding block **80** is positioned above the tape T, and the collection block **100** is positioned below the tape T and an interspace is provided between the two blocks for the passage of the tape. The collection block **100** is connected on the front face of the front upright member **20** by any suitable coupling means such as screws **116**. Positioned between the block **80** and the block **100** is a thermal insulator or spacer formed of thermal insulating material **118**, and positioned between the front face of the front upright member **20** and the block **80** is another thermal insulator or spacer formed of thermal insulating material **120**. Both thermal insulators **118** and **120** may suitably be formed from asbestos.

The lower portion **110** of the collection block **100** is provided with a well portion **122** which surrounds an anode insulator **124**. The anode insulator receives a screw **112** which passes through the base of the well portion **122** for fixedly coupling thereto the anode insulator. The end of the anode insulator **124** remote from the well portion receives the anode **106** which suitably is made in the form of a screw. Screw **112** and the anode insulator **124** are effective to hold the anode **106** in contact with the underside of tape T. In order to insure proper contact between the anode **106** and the underside of tape **7**, the anode **106** may be adjusted with respect to the anode insulator **124**. A transformer **126** and the high voltage supply **57** are carried on the rear of the front upright member **20** to supply a high voltage of at least 3000 volts, and preferably 4000 volts to the anode **106** through connecting lead **130**, which connects the output of the high voltage supply **57** to the anode **106**. The high voltage supply **57** includes a group of rectifiers and condensers to rectify and step-up the voltage output from the transformer **126**.

As the inert gas stream has a charge which varies from neutral to a highly negative state, a positive charge from the anode is effective to attract the material or particulate matter attached to the radioactive isotope to the tape T as it moves past the anode. The particles in the particulate matter coming off the column are fine particles. The positive charge from the anode is effective to pull the particles against the tape T to overcome the natural tendency of the particles to rise as a result of the heated gas stream.

It is also possible to take the vapor and impart a negative charge thereto so that the anode which is positively charged will be more effective to cause the oppositely charged material to migrate to the tape T and be captured thereby.

The moving tape T which is capable of recording, storing and providing an indication of the presence of the radioactive isotope is prepared from a standard transparent Mylar film which is about 0.5 mil thick and is coated with a mixture of anthracene and a polyester, such as acrylic. The anthracene performs the function of a scintillation phosphor and the acrylic is used to bind or bond the anthracene to the Mylar tape. The scintillation phosphor is effective to provide a highly effective means of counting weak beta-emitting isotopes and gamma emitting isotopes.

For certain purposes, it may be desirable to effect a strong bond between the anthracene and the Mylar film, whereby to effect better readings from a counting device. A strong bond is desirable where the tape will be read soon after it has captured the radioactive isotope. However, for those purposes where it is intended to store the tape for a period of time and then read the tape at a later time, a stronger bond is desirable. With the stronger bond, which is obtained as explained subsequently, a durable, permanent record is obtained; this permanent record which is achieved with the stronger bond is not susceptible to contamination or physical damage. In order to effect stronger bond, it is proposed to apply a second coat of the polyester, such as the acrylic, to the tape.

It is known that anthracene has as one of its properties, the ability to emit photons when bombarded with beta or gamma particles. However, the photon emitting properties of the anthracene when coated onto the Mylar film in accordance with this invention now provides for the storing of the isotope, so that the tape may then be passed through the counting device (not shown) to determine the quantity of the radioactive isotope stored in

addition to the mere presence thereof and thereby the quantity of and presence of the radioactive isotope forming part of the particulate matter carried by the inert gas stream. In this respect, it is to be noted that the radioactive isotope always emits radioactive particles.

If it is assumed that the compound or material under study contains the constituents A, B, C, D and E—the tag or radioactive isotope may be one of the aforesaid constituents, or tag may be introduced into the compound and attach itself to one or more of the constituents and replace its non-isotopic form. Where the tag forms one or more of the constituents A, B, C, D, E, the tag is detected, collected or stored in accordance with the present invention and based upon its time of exiting from the column of the gas-liquid chromatographic apparatus, the radioactive constituent or constituents is ascertained. Where the tag is introduced into the compound, it will attach itself to one or more of the constituents A, B, C, D and E, and knowing the quantity of the tag introduced the quantity in addition to the presence of the tag attached to one or more of the constituents can be continuously and individually ascertained.

It is preferred to use a Mylar film known as "Chronor" and which is manufactured by and obtainable from the Du Pont Company of Wilmington, Delaware. This film is a 35 mm. double perforated film and may suitably be used in conjunction with the tape transport mechanism 10. Anthracene is a scintillating material which is obtainable from the Eastman Kodak Company of Rochester, New York.

One method of forming or preparing the tape T which includes the anthracene bonded to the Mylar film according to this invention is as follows:

A solution of light toluene is placed into a container to act as a solvent. Anthracene is added to the toluene solution, and then the polyester, such as the acrylic, is added to the solution of toluene and anthracene. The Mylar film is then passed through the solution containing the toluene, anthracene and acrylic so as to bond the anthracene to the Mylar film whereby to form the tape T and render it suitable for energization by the radioactive isotope and responsive thereto to store and record the presence and/or quantity of the radioactive isotope present in the inert gas stream. After the Mylar film is withdrawn from the solution of toluene, anthracene and acrylic, the toluene evaporates and an even coating of the anthracene is bonded to the Mylar film by the acrylic to form the tape T.

Another method of preparing the tape T having the anthracene bonded to the Mylar film according to the invention is as follows, and this method is the preferred method:

The uncoated Mylar film as obtained from the Du Pont Company is bonded to a flat clean surface by means of any suitable bonding tape or material; the bonding tape is only lapped to the edge performations of the film and preferably does not extend beyond the perforations towards the center of the film.

The exposed film surface is then roughened by any suitable abrasive means, such as sandpaper.

The polyester, such as the acrylic is then sprayed onto the roughened surface of the film to form a thick damp coating of the polyester on the roughened surface of the film.

A pasty material, such as an acrylic spray, together with the anthracene is then sprinkled onto the thick damp coating of the polyester. The acrylic spray may suitably be dispensed from an aerosol container onto the thick damp coating.

The film having its face coated with the polyester and anthracene is then allowed to stand, set or remain for a short time, preferably ten (10) minutes to set the anthracene onto the film by means of the polyester.

After the anthracene has been set onto the film, the film is removed from the flat surface, and any excess

anthracene not bonded to the film is removed by shaking the film.

The film with the anthracene bonded thereto forms the tape T and is now ready for use or exposure in the small particle device to collect, record and store the radioactive isotope.

After the tape T is prepared in accordance with either of the aforesaid methods and used with the small particle collection device to record and store the radioactive isotope, the present invention includes the following method for providing a permanent record on the exposed tape T and prevent contamination of the tape and/or loss of any indication of the presence and quantity of the radioactive isotope in the inert gas stream.

The method of treating the exposed tape T to provide a permanent record is as follows: The exposed tape T is sprayed with a solution of saturated anthracene benzyl solution, preferably an atomized solution. Allow the anthracene benzyl solution sprayed tape to stand for about three (3) minutes. Then fix the tape by spraying the tape with a top coat of a polyester, such as an acrylic to prevent further flaking or contamination, and thereby obtain a fixed record which is stored on the tape.

After the tape T has been prepared as set forth above to provide a permanent record, it may be fed to a counting device (not shown) which will detect the presence and quantity of the radioactive isotope present in the inert gas stream. The tape T may be fed immediately to the counting device or it may be stored for any period of time and then fed to the counting device and accurate results will be obtained indicating the presence and quantity of the radioactive isotope in the inert gas stream.

While there has been described what is at present considered the preferred embodiments of the invention, it will be apparent that various changes and modifications may be made therein without departing from the scope of the invention.

What I claim is:

1. A small particle collection and detection apparatus for the continuous collection and detection of a radioactive isotope in the effluent on a moving tape adapted to collect, detect and store the radioactive isotope, the effluent exiting from a packed column of gas-liquid chromatography apparatus and consisting of particulate matter coupled to the radioactive isotope and particulate matter uncoupled to the radioactive isotope, comprising tape transport means adapted to support and transport the tape in a predetermined time relationship related to the time of exiting of the effluent from the packed column, said tape being adapted to receive said radioactive isotope and particulate matter coupled to said radioactive isotope, feeder means operatively connected with said tape transport means for feeding the effluent to the tape, said tape having edge engagement portions, said tape transport means including tape edge engaging means adapted to engage solely the edge engagement portions of the tape whereby to prevent contamination thereof, and transferring means operatively associated with said feeder means for transferring the portion of the effluent consisting of the particulate matter coupled to the radioactive isotope onto the portion of the tape between the edge engagement portions thereof.

2. Apparatus according to claim 1, wherein said tape transport means includes a pair of rotatable sprockets positioned on opposite sides of said feeder means, each of said sprockets being provided with peripheral teeth adapted for engagement with the edge engaging portions of said tape, one of said sprockets being a drive sprocket and the other of said sprockets being a driven sprocket, motive means coupled to said one sprocket for rotation thereof to move the tape in said predetermined time relationship, an L-pad for each said sprocket movable into and out of engagement with its associated sprocket for holding the tape to said sprockets and movable therewith when said L-pads are in engagement with said sprockets,

switch means operatively connected with said motive means for control thereof, and means coupled with said switch means engageable by one of said L-pads when out of engagement with its associated sprocket for deenergizing said motive means, thereby stopping the rotation of said sprockets and movement of the tape.

3. Apparatus according to claim **1**, comprising support means, means forming part of said support means for positioning said feeder assembly above the tape, said tape transport means being carried by said support means for transporting the tape tranversely to said feeder assembly, said feeder assembly including a casing element having three chambers in heat-exchange relationship to each other a tube having one end coupled to the exit of the packed column and having the other end opening onto the tape carried within one of said chambers, a thermostatic sensing means in the second of said chambers, a heater carried in the third of said chambers to maintain the effluent heated as it passes through said tube, said thermostatic sensing means being responsive to the temperature of said chamber to activate said heater to maintain a substantially constant temperature in said tube.

4. A small particle collection and detection apparatus for the continuous collection and detection of a radioactive isotope in the effluent on a moving tape adapted to collect, detect and store the radioactive isotope, the effluent exiting from a packed column of gas-liquid chromatography apparatus and consisting of particulate matter coupled to the radioactive isotope and particulate matter uncoupled to the radioactive isotope, comprising tape transport means adapted to support and transport the tape in a predetermined time relationship related to the time of exiting of the effluent from the packed column, feeder means operatively connected with said tape transport means for feeding the effluent to the tape, transferring means operatively associated with said feeder means for transferring the effluent consisting of the particulate matter coupled to the radioactive isotope onto the tape, support means, means forming part of said support means for positioning said feeder assembly above the tape, said tape transport means being carried by said support means for transporting the tape transversely to said feeder assembly, said feeder assembly including a casing element having three chambers in heat-exchange relationship to each other, a tube having one end coupled to the exit of the packed column and having the other end opening onto the tape carried within one of said chambers, a thermostatic sensing means in the second of said chambers, and a heater carried in the third of said chambers to maintain the effluent heated as it passes through said tube, said thermostatic sensing means being responsive to the temperature of said chamber to activate said heater to maintain a substantially constant temperature in said tube.

5. Apparatus according to claim **4**, said transferring means including an anode assembly coupled to said support means, said anode assembly including a collection block and a holding block coupled thereto, said collection block being fixed to said support means below the tape, said holding block being fixed to said support means above the tape, a thermal insulator interposed between said holding block and said support means and between said holding block and said collection block, an anode held in position beneath the tape by said collection block, adjustable means coupling said anode to said collection block to move said anode into contact with the tape, and recirculating cooling water passageways to assist in the precipitation of the particulate matter coupled with the radioactive isotope onto the tape.

6. Apparatus according to claim **1**, said feeder assembly including first, second and third casing members coupled in heat exchange relationship to each other, a tube adapted to carry the effluent positioned in said first casing, said tube having one end extending outside said first casing and being coupled to the packed column and having its other end positioned above the tape for carrying thereto the effluent, a heater positioned in said second casing for maintaining the effluent in said tube heated to a temperature of about 225° C. to prevent condensation of the particulate matter in the effluent, control means coupled with said heater for control thereof and variable to maintain the 225° C. temperature in said tube, a thermostatic sensing element positioned in said third casing member connected with said control means for communicating the temperature in said tube to said control means, and a block coupled to said first casing and in heat-exchange relationship therewith, said block being positioned above the tape and having an opening, said other end of said tube passing through said opening for positioning above the tape.

7. A small particle collection and detection apparatus for the continuous collection and detection of a radioactive isotope in the effluent on a moving tape adapted to collect, detect and store the radioactive isotope, the effluent exiting from a packed column of gas-liquid chromatography apparatus and consisting of particulate matter coupled to the radioactive isotope and particulate matter uncoupled to the radioactive isotope, comprising tape transport means adapted to support and transport the tape in a predetermined time relationship related to the time of exiting of the effluent from the packed column, feeder means operatively connected with said tape transport means for feeding the effluent to the tape, said feeder means including first, second and third casing members coupled in heat exchange relationship to each other, a tube adapted to carry the effluent positioned in said first casing, said tube having one end extending outside said first casing and being coupled to the packed column and having its other end positioned above the tape for carrying thereto the effluent, a heater positioned in said second casing for maintaining the effluent in said tube heated to a temperature of about 225° C. to prevent condensation of the particulate matter in the effluent, control means coupled with said heater for control thereof and variable to maintain the 225° C. temperature in said tube, a thermostatic sensing element positioned in said third casing member connected with said control means for communicating the temperature in said tube to said control means, a block coupled to said first casing and in heat-exchange relationship therewith, said block being positioned above the tape and having an opening, said other end of said tube passing through said opening for positioning above the tape, and transferring means operatively associated with said feeder means for transferring the effluent consisting of the particulate matter coupled to the radioactive isotope onto the tape.

8. A small particle collection and detection apparatus for the continuous collection and detection of a radioactive isotope in the effluent on a moving tape adapted to collect, detect and store the radioactive isotope, the effluent exiting from a packed column of gas-liquid chromatography apparatus and consisting of particulate matter coupled to the radioactive isotope and particulate matter uncoupled to the radioactive isotope, comprising tape transport means adapted to support and transport the tape in a predetermined time relationship related to the time of exiting of the effluent from the packed column, feeder means operatively connected with said tape transport means for feeding the effluent to the tape, said feeder means including first, second and third casing members coupled in heat exchange relationship to each other, a tube adapted to carry the effluent positioned in said first casing, said tube having one end extending outside said first casing and being coupled to the packed column and having its other end positioned above the tape for carrying thereto the effluent, a heater positioned in said second casing for maintaining the effluent in said tube heated to a temperature of about 225° C. to prevent condensation of the particulate matter in the effluent, control means coupled with said heater for control thereof

and variable to maintain the 225° C. temperature in said tube, a thermostatic sensing element positioned in said third casing member connected with said control means for communicating the temperature in said tube to said control means, a block coupled to said first casing and in heat-exchange relationship therewith, said block being positioned above the tape and having an opening, said other end of said tube passing through said opening for positioning above the tape, transferring means operatively associated with said feeder means for transferring the effluent onto the tape, support means, means forming part of said support means for positioning said feeder assembly above the tape, said tape transport means being carried by said support means for transporting the tape transversely to said feeder assembly, said feeder assembly including a casing element having three chambers in heat-exchange relationship to each other, a tube having one end coupled to the exit of the packed column and having the other end opening onto the tape carried within one of said chambers, a thermostatic sensing means in the second of said chambers, and a heater carried in the third of said chambers to maintain the effluent heated as it passes through said tube, said thermostatic sensing means being responsive to the temperature of said chamber to activate said heater to maintain a substantially constant temperature in said tube.

9. Apparatus for the continuous collection of material on a moving tape, the material including particulate matter and, particulate matter with a radioactive isotope coupled thereto in the effluent leaving a column of gas-liquid chromatographic apparatus, comprising an anode assembly including means for precipitating the material onto the tape, a feeder assembly adapted to convey the effluent from the chromatographic apparatus to the tape including means maintaining the temperature of the effluent constant, and tape transport means adapted to move the tape past the anode assembly in predetermined time relationship related to the time of exiting of the effluent from the column, said precipitating means including cooling means to condense the effluent supplied by said feeder assembly and potential means to attract the material onto the tape, said anode assembly including a holding block and a collection block, said tape transport means including support means, tape drive means carried by said support means, power means carried by said support means, means coupling said collection block to said support means below the tape, means thermally and insulatingly coupling said holding block to said support means and said collection block above the tape to provide an interspace between said blocks for the passage of the tape, a passageway in said holding block, said feeder assembly being coupled to said holding block for transferring the material to the tape through said passageway, an anode aligned with said passageway, means insulatingly coupling said anode to said collection block, said power means providing a potential of at least 3,000 volts, means coupling said potential to said anode to precipitate the material electrostatically.

10. Apparatus according to claim **9**, wherein said power means provides a potential of about 4000 volts, said collection block includes recirculating water passageways and coupling orifices connected with said water passageways for recirculating cooling water therethrough to condense the particulate matter as it exits from said feeder assembly, said collection block having a well portion, said insulating means including an insulator positioned in said well portion, means coupling said insulator to said collection block, and said anode including a screw portion carried by said insulator and adjustable therein for movement into contact with the tape.

11. Apparatus according to claim **10**, said feeder assembly comprising a tube having an input end connected with the output of the column and an output end, passing through said passageway of said holding block and held thereby in registry with said anode above the tape, a

thermostatic sensing element and a heater maintained in heat exchange coupling with said tube for maintenance thereof heated to a substantially constant temperature of 225 C., a calibration device coupled with said sensing element and said heater responsive to said sensing element for rendering said heater operative to maintain said temperature, said insulating means including a thermal insulator preventing said support means and said collection block from being heated to said temperature, and said tape transport means including moving means, means adapted to grip solely the edges of the tape for transport thereof transversely to said feeder assembly and said anode assembly by said moving means, and switch means adapted to deenergize said moving means responsive to said gripping means releasing the edges of the tape, the tape being a Mylar film coated with a mixture of anthracene and a polyester.

12. Apparatus for feeding an effluent derived from a packed column comprising particulate matter and a radioactive isotope and precipitating the particulate matter coupled to the radioactive isotope, comprising means to maintain the temperature of the effluent at substantially the same temperature as in the packed column after removal therefrom and including thermostatic sensing means, a feeder to remove the effluent from the packed column, a heater in heat exchange relationship to said feeder along the length thereof, said sensing means including means to sense the temperature along said length for activating said heater to maintain the effluent at the temperature of said temperature of the material in the packed column, and precipitation means including a cooling means and high potential means to precipitate the particulate matter coupled to the radioactive isotope by cooling and electrostatic precipitation.

13. A tape for recording, storing and providing an indication of the presence of a radioactive isotope, comprising a transparent Mylar film about 0.5 mil thick, a first coating of a mixture of a scintillation phosphor providing a highly effective means for counting weak beta-emitting isotopes and gamma-emitting isotopes toluene to insure uniform coverage of said anthracene onto said film and capable of evaporating, and an acrylic polyester to bond said anthracene uniformly to said film upon evaporation of said toluene, and a second coating of an acrylic polyester on said first coating.

14. A method of forming a tape having anthracene uniformly bonded to the surface of the tape for the recording and storing of a radioactive isotope, a Mylar film coated with a mixture of anthracene and an acrylic, the method including the steps of adding anthracene to a toluene solution to form a solution of anthracene and toluene, adding an acrylic to the anthracene-toluene solution, passing the film through the solution of acrylic-anthracene-toluene so as to bond the anthracene to the film and then withdrawing the film from the last-mentioned solution to form an even coating of anthracene bonded to the surface of the film upon evaporation of the toluene which forms said tape.

15. A method of preparing a tape responsive to a radioactive isotope and adapted for the storing thereof, comprising the steps of roughening the surface of a transparent polyester film, spraying a polyester onto the roughened surface of the film to form a thick damp coating, sprinkling a scintillation phosphor together with a polyester aerosol spray onto said thick damp coating, permitting the film to set for about ten minutes to set the scintillation phosphor onto the film, and then removing excess scintillation phosphor from the film.

16. A method of forming a tape responsive to radioactive isotope activation, comprising the steps of roughening the surface of a transparent polyester film while maintained in a flat condition, forming a thick damp coating on said roughened surface by spraying a polyester thereon, sprinkling a pasty material together with a scintillation phosphor onto said damp coating, setting the film

coated scintillation phosphor by permitting it to stand for a short period of time, and then shaking said coated film to remove excess scintillation phosphors.

17. A method of treating a tape formed in accordance with claim **16** after exposure to a radioactive isotope for storage thereof on said tape to provide a permanent record, comprising the steps of: spraying said exposed tape with a saturated anthracene benzyl solution, setting the benzyl solution sprayed tape, and fixing the tape by applying a top coat of a polyester to prevent further flaking or radioactive isotope activation whereby to obtain a fixed record which is stored on the tape.

18. A method according to claim **17**, wherein the tape is sprayed with an atomized solution of saturated anthracene benzyl, and the tape is set by allowing it to stand for about three minutes.

19. A small particle collection and detection apparatus for the continuous collection and detection of a radioactive isotope in the effluent on a moving tape comprising a Mylar film coated with a mixture of anthracene and a polyester, said tape having side edge engagement means and being adapted for the collection, detection and storing of the radioactive isotope, the effluent exiting from a column of gas-liquid chromatography apparatus and consisting of particulate matter coupled to the radioactive isotope and particulate matter uncoupled to the radioactive isotope, comprising tape transport means adapted to support and transport the tape in a predetermined time relationship related to the time of exiting of the effluent from the column, said transport means including tape edge engaging means for engaging solely the edges of the tape at said side edge engagement means, feeder means operatively connected with said tape transport means for feeding the effluent to the tape, and transferring means operatively associated with said feeder means for transferring the effluent consisting of the particulate matter coupled to the radioactive isotope onto the tape.

20. A method of forming a tape having uniformly bonded thereto on the surface thereof a scintillation phosphor for the recording, storing and providing of an indication of the presence of a radioactive isotope comprising a transparent polyester film coated with a mixture of a scintillation phosphor and a polyester, the method including the steps of: adding a scintillation phosphor to a solution of toluene to provide a solution of toluene-scintillation phosphor, adding a polyester to said last-mentioned solution to provide a solution of polyester-toluene-scintillation phosphor, passing a transparent polyester film through the last-mentioned solution to coat the film uniformly on the surface thereof with said toluene, polyester and scintillation phosphor, evaporating said toluene from the surface of said film whereby to leave a uniform continuous coating of the scintillation phosphor on the surface of the film bonded thereto by the polyester, and applying a coating of polyester onto the film coated with the scintillation phosphor and polyester, thereby effecting a strong bond between the surface of the film and the scintillation phosphor.

21. Apparatus for the continuous collection on a moving tape of particulate matter and particulate matter coupled to a radioactive isotope in the effluent leaving a column of gas-liquid chromatographic apparatus, comprising an anode assembly including means for precipitating the particulate matter and the particulate matter coupled to the radioactive isotope onto the tape, a feeder assembly adapted to convey the effluent from the chromatographic apparatus to the tape including means maintaining the temperature of the effluent constant, said feeder assembly including an exit portion, said anode assembly including an anode, in registry with said exit portion to precipitate the particulate matter and the particulate matter coupled to the radioactive isotope onto said tape immediate to said anode and tape transport means adapted to move the tape past the anode assembly in predetermined time relationship related to the time of exiting of the effluent from the column, said precipitating means including cooling means to condense the effluent supplied by said feeder assembly and potential means to attract the particulate matter and the particulate matter coupled to the radioactive isotope onto the tape.

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