Jan. 2, 1968 D. L. PETITJEAN ETAL 3,361,908

METHOD AND APPARATUS FOR ELECTRON ATTACHMENT DETECTION

Filed Jan. 3, 1964 2 Sheets-Sheet 1

Fig. 1

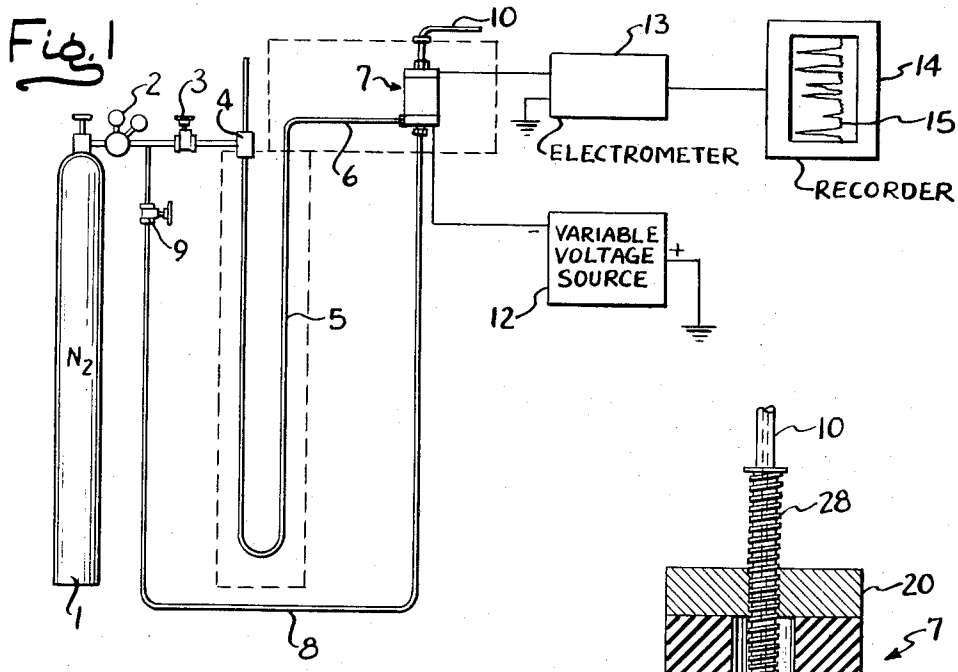

Fig. 2

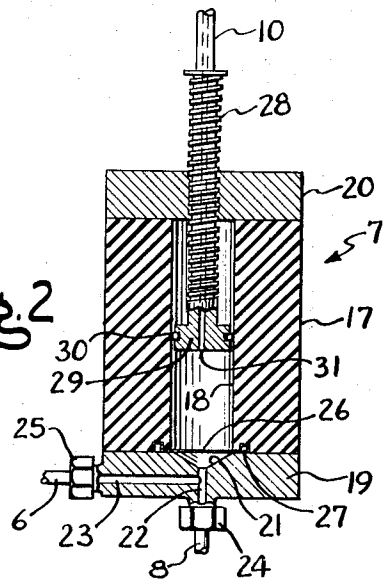

Fig. 3a

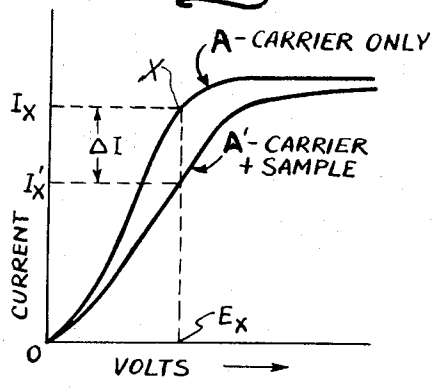

Fig. 3b

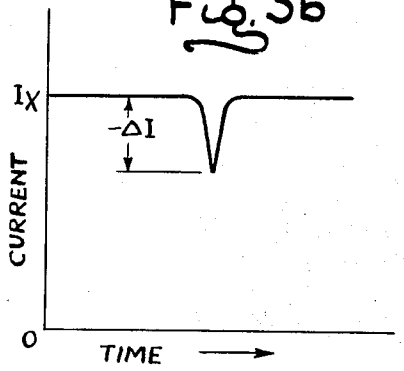

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Fig. 4a

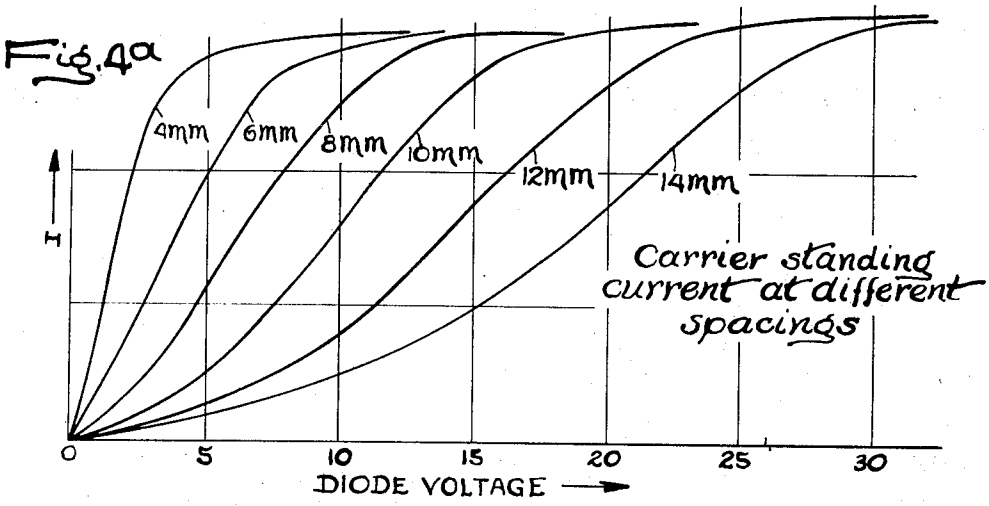


Fig. 4b

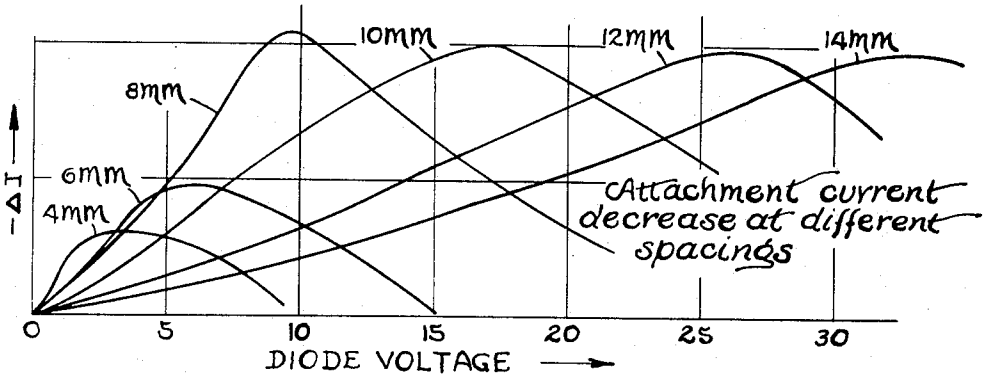
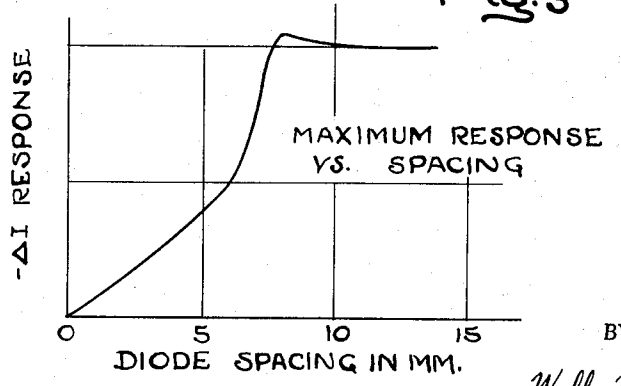


Fig. 5



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United States Patent Office 3,361,908
Patented Jan. 2, 1968

3,361,908

METHOD AND APPARATUS FOR ELECTRON ATTACHMENT DETECTION

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Filed Jan. 3, 1964, Ser. No. 335,503
7 Claims. (Cl. 250—43.5)

This application relates to an improved process and apparatus for quantitative analysis of electronegative gases in processes employing electron attachment phenomena.

In gas chromatography gaseous components of an organic gas or vaporized sample are separately eluted at time-spaced intervals in a carrier gas stream from a chromatographic column for subsequent qualitative and quantitative analysis. These techniques are spectacularly successful in separating a great variety of components present in amounts from major proportions to mere traces in a single sample. The successful resolution of different given components is determined in part by the available selection of absorbing agents for packing or coating internal column surfaces so that in effect different delay times are established for different components of the sample introduced into the carrier gas stream flowing through the column. While successful resolution for qualitative analysis can usually be accomplished by multiple separations with different combinations of absorbing agents, reliable quantitative analysis of a selected component is rendered especially difficult by reason of the widely varying amounts or concentrations presented for measurement in different samples.

A particularly sensitive detection mode for certain gases which have an attraction for electrons (sometimes referred to as electronegative gases) and one with which the present invention is exclusively concerned, utilizes measurement of the amplitude or duration and amplitude of an ion current change produced while subjecting the gas stream to a source of ionizing radiation. More particularly, this invention is concerned with an electron attachment mode of detection in which a reference electron current level is largely established by ionization of the carrier gas and significantly decreased by attachment of electrons to molecules of electronegative gases to be measured. Ideally, the maximum current deviation from the reference level is linearly proportional to the maximum concentration of molecules of the electronegative sample swept through the detector by the carrier which maximum concentration in turn should with good column separating performance linearly vary with the quantity of that component in the sample. The opportunities for departure from linearity as well as variation from a known calibration are almost endless. Rather arbitrary conditions have therefore necessarily been adhered to in order to effect a calibration and reproduce or compare results.

It is an object of the present invention to provide a simple but effective method and apparatus for measuring an electronegative gas compound in a carrier gas stream with an optimum balance of sensitivity and linearity.

More particularly, it is an object to provide a method for measuring a quantity of an electronegative gas in a carrier gas stream with optimum sensitivity in an electron attachment detection mode.

It is another object to provide a method for determining optimum conditions for linear response in an electron attachment mode, and a further object to provide a method of measuring a wide range of electronegative sample concentrations with linear response in an electron attachment mode.

It is a further object to provide means for adjusting the electrode spacing in an electron attachment detector diode for optimizing response to small concentrations of an electronegative gas in a carrier stream.

Various other objects and advantages will become apparent as the following detailed description proceeds taken together with the accompanying drawings in which

FIGURE 1 is a schematic diagram of a chromatograph detection system utilizing the practice of the invention.

FIG. 2 is a cross-section view of the diode detector employed in the system of FIGURE 1.

FIG. 3*a* is a curve relating ionization current to diode voltage for the carrier gas.

FIG. 3*b* is a curve showing the variation of detector current with time as a sample component peak passes through the detector.

FIG. 4*a* is a family of curves of carrier standing current plotted against voltage for different diode spacings.

FIG. 4*b* is a family of curves of attachment current response plotted against voltage for different electrode spacings under conditions similar to those of FIG. 4*a*.

FIG. 5 is a curve relating attachment current response maxima to diode spacing.

While the invention is described in connection with the preferred embodiments thereof it will be understood that the invention is not to be limited to the specific embodiment shown and described, and that the appended claims are intended to cover the various alternative and equivalent constructions within the spirit and scope of the invention.

An ionization detection system for measurement of an electronegative gas component in a carrier gas is schematically illustrated in FIGURE 1. As shown therein a carrier gas, preferably nitrogen, is supplied from a tank **1** at a predetermined pressure, as set by a pressure regulator **2** through an inlet valve **3** and sample injection chamber **4** to the inlet end of a chromatographic column **5**. The column illustrated is of a packed type in which the liquid phase is coated on small solids packed into the column tubing. Columns of various diameter and lengths and with various types of packing materials and liquid phase absorbing agents are known in the art and selected to best separate the particular gases involved. In many instances a very small diameter or capillary column is employed in which the liquid phase is supported solely on the inner walls of the tubing itself. The sample may be injected into the carrier stream by various methods also known in the art. When, for example, the sample is mainly liquid, the sample chamber or part of it is maintained at a sufficiently high temperature to instantly vaporize the sample and facilitate the complete introduction of the sample as a gas into the carrier gas stream in a very small time interval. At the output end of the column, the effluent consists of a carrier gas with successively appearing peaks of separated sample components. This effluent is supplied through a line **6** to the inlet end of an ionization diode detector cell **7**. In instances where it is desired to decrease the residence time of effluent flowing through the detector, an additional amount of carrier gas is introduced in the inlet end of the detector through a scavenge line **8** connected to the carrier gas tank through a valve **9**. In most instances the flow rate is fast enough when a packed column instead of a capillary column is employed, and the valve **9** is closed or the scavenge line is removed and the scavenge inlet is closed. The column effluent, mixed with whatever scavenge gas may be added, flows through the detector **7** and exits at the top through a tube **10** usually vented to atmosphere except when the effluent is to be collected or its flow measured. The broken-line enclosures for the column and cell indicate that each may be maintained in an elevated ambient temperature medium to prevent condensation of the sample components.

The respective ends of the detector cell **7** are connected as diode terminals in circuit with an adjustable direct cur-

rent voltage source 12 and an electrometer 13 or other very sensitive current measuring device. As further shown in FIGURE 1, the detector anode is connected to an input terminal of the electrometer 13 and the detector cathode is connected to the negative terminal of the supply 12 which suitably may have a maximum voltage of 50 volts and for which calibrated adjustment in at least the 5 to 30 volt range should be easily and accurately available. The positive terminal of the supply 12 and the other electrometer input terminal are grounded to complete the circuit to the detector anode. The current amplitudes involved are very small, being often less than 10^{-12} amperes, and the current measuring instrument is selected accordingly. Inasmuch as the signal amplitude varies with time due to the time-varying amounts of sample component in the carrier, the current values are preferably plotted against time in a recording instrument 14. The plot 15 shown in the vertically moving strip of the recorder 14 is by definition a chromatogram inasmuch as the successive current peaks rising from the base level are a measure of the amplitudes of the successive separated sample components.

As further shown in FIG. 2 and in accordance with the invention, the detector 7 has an ionization chamber in which the electrode spacing and the chamber volume are simultaneously adjustable over a significant range. A chamber of constant cross-section dimension along its length is defined by a cylindrical bore 18 in an insulating body 17 which is suitably made of glass-supported Teflon (glass fibers embedded in solid polytetrafluoroethylene.) The structural end supports for the chamber are stainless steel disks or end caps 19, 20 which are tightly secured to each end of the insulating body 17, suitably by mounting screws (not shown). The end caps themselves as the external electrode terminals must remain insulated from each other. The lower end cap 19 has a central concave recess 21 facing the chamber bore 18 and a small central scavenge bore 22 extends axially through its remaining thickness. An intersecting radial bore 23 in end cap 19 facilitates supply and mixing of the column effluent with the scavenge gas. Fittings 24, 25 at the ends of the small inlet bores may be provided for convenient connection to the tubing lines 6 and 8.

The lower electrical end wall of the chamber 18 is defined by a disk of stainless steel foil 26 having small distributed perforations and clamped between the lower end cap 19 and the insulating body 17. Prevention of gas leakage is assured by a resilient O-ring gasket 27 carried in a groove in the lower end of the insulator 17 and having an inside diameter somewhat larger than the foil disk. The foil surface is thus maintained planar and perpendicular to the chamber axis. The inlet gas behind the foil in the concave recess 21 diffuses through the distributed perforations in the foil to enter the chamber 18.

To provide an upper electrical end wall of the chamber, the end cap 20 is bored and threaded to receive a stainless steel screw 28 with an enlarged piston-like lower end 29. The lower face of the piston is a planar surface facing and parallel to the foil surface. These facing surfaces are the effective electrode surfaces of the diode. The distance between them is the diode spacing, and it is adjusted by turning the screw 28. A groove and O-ring 30 in the wall of the piston 29 seals the bore 18 against gas flow around the electrode to both prevent unpredictable operation due to extended residence time of gas in the chamber and a varying outlet orifice along the threaded screw 28. Instead, the screw 28 has a small axial bore 31 through which the gas flows to the vent tube 10. For convenience, the screw lead is established at an integral dimensional unit so that the exposed threads can be counted to easily determine the precise electrode spacing without disassembling the detector. In a specific embodiment corresponding to that of FIG. 2 with a one centimeter chamber diameter, an electrode spacing up to 25 millimeters is provided with electrode screw lead per turn of exactly one millimeter.

To provide a constant ionizing source unaffected by the volume change of the detector upon adjustment of the electrode spacing, radioactive material is incorporated in the upper surface of the foil. The ionizing radiation source is preferably tritium (^3H) which can be concentrated as a relatively high strength source in a layer of titanium on the foil. Thus for a one-centimeter diameter chamber, a source having an activity of approximately 300 millicuries serves to ionize the gas passing through the foil perforations. Tritium also desirably has short range radiation (as compared to radium, for example) which permits maximum ionization and therefore maximum attachment response at short electrode spacings and thus helps minimize residence time of the gas passing through the detector. For example, the most effective ionizing range of the electrons constituting the beta radiation of tritium in nitrogen near atmospheric pressure (gas pressures in the cell are usually above but near atmospheric pressures) is from six to ten millimeters. For radium the range of alpha radiation would be closer to 32 millimeters.

In the operation of an electron attachment detector pure nitrogen carrier gas flowing through the perforated cathode 26 towards the opposing anode surface 29 is subjected to the beta emission of the tritium source. The radiated electrons ionize a portion of the nitrogen molecules to produce relatively low energy electrons and positive ions. With the relatively weak electric field as provided by around 15 volts across electrodes of, for example, 8 millimeter spacing, most of the electrons are collected at the anode but are not sufficiently accelerated to produce appreciable further ionization. When the voltage is lowered, not all of the electrons are attracted to the anode and the ion current will vary more or less directly with the applied low voltage.

Such a nitrogen standing current vs. voltage characteristic is shown in FIG. 3*a*, Curve A. As may be seen, the ion current flowing through the electrometer input circuit increases from zero at zero volts until it reaches a fairly well defined plateau beyond which an increase in voltage causes practically no increase in current. The knee of the curve is more or less sharply defined, and the voltage level at which the plateau is reached depends to some extent upon the purity of the nitrogen source and the over-all cleanliness of the system. The dimensions of the current ordinarily depend primarily upon the amount of radioactive material, the electrode spacing, the applied voltage, and to some extent upon the number of nitrogen molecules in the chamber, which in turn depend upon the pressure and temperature. Other gases may also be employed as the carrier, but nitrogen is preferred both because of its general suitability as a column carrier gas and because it is neither appreciably electronegative nor subject to metastable excitation (as would be argon, for example). The metastable excitation effects may be very advantageously used, but in a higher voltage mode of operation than that peculiar to the electron attachment mode.

When a strongly electronegative sample component is carried by the nitrogen—and halogenated organic compounds employed as pesticides are typical of such compounds whose concentration is particularly well analyzed by electron attachment methods—the electrons produced by the beta radiation are attached to a greater or lesser extent to the electronegative molecules. Fewer electrons are collected therefore at the anode for a given applied electrode voltage. The negative ions formed by addition of an electron to an electronegative molecule or atom recombine at a very much higher rate than do the electrons with the positive ions formed by the beta radiation so that the ion current collected at the electrodes remains largely limited to those electrons escaping attachment.

The total ionization current for nitrogen mixed with an electronegative gas also increases with voltage at low values until the further voltage increase has a much

smaller effect in increasing current as shown in Curve A' of FIG. 3*a*. To the extent that Curve A' has a knee, that knee occurs at a higher voltage than that of Curve A for the carrier gas alone (at least this has been so for all electronegative gases thus far tested by us). It should also be appreciated that portraying Curve A' to the same current scale as Curve A designates a particular concentration of the electronegative gas out of a very wide range likely to be encountered. While the quantity of electronegative gas present in the chamber is typically only a very small proportion of the carrier plus sample component mixture, the maximum concentration of the sample component itself likely to be encountered in one series of tests may well be a thousand times greater than in another series. This range of variation of concentration is a very important factor to be taken into account in determining flow and voltage and other conditions for satisfactory sensitivity and linearity in electron attachment measurement systems.

In usual operation, it has been the practice in the art to select a voltage operating point at or somewhat below the knee of the carrier standing current curve in the interest of sensitivity. Point X on the carrier current Curve A of FIG. 3*a* is such a point, and voltage E_x produces a carrier gas standing or reference current I_x. When the sample is present of the kind and quantity to produce the Curve A' of FIG. 3*a*, a lesser current I_x' is measured by the electrometer for the same applied voltage E_x. The decrease in current ΔI varies linearly with the amount of the particular sample gas under certain important conditions.

Looking to FIG. 3*b*, which shows the change of collected ionization current with time, the carrier standing current at the constant applied voltage E_x remains at the value I_x so long as the carrier gas only passes through the detector chamber. The current decreases by an increment ΔI and rises again as an electronegative sample peak resolved by the column passes through the detector. Using the carrier standing current level as a baseline the sample peak can be oriented either negatively or positively in an indicating display to provide a measure of the electronegative gas concentration. If the column has provided an optimum resolution, the amplitude of the peak is a sufficient measure of sample concentration. Under some other column conditions the time-current integral may be a more reliable measure of concentration. If several electronegative compounds are present in the sample, several peaks will be detected as indicated in the chromatogram 15 of FIGURE 1. For each of the peaks, a different calibration multiplier for determining the molar amount of the particular sample component per current increment may be required (different gases have different electronegative characteristics) but no further problem is involved if conditions for linearity are maintained and the sensitivity is sufficient.

As a general rule, a linear relationship between the attachment deviation current ΔI and the number of molecules of a particular electronegative gas present in the conveying chamber is maintained so long as the deviation current does not exceed from about ⅓ to ½ of the carrier standing current at the same voltage. This finding is difficult to demonstrate in terms of explanation of the mechanism involved, but is well verified experimentally. The practical effect is that concentrations of the sample gas to be measured must be limited in some instances. This is easily enough done by decreasing or diluting the sample to be separated in the column or by diluting the column effluent. Thus for a series of samples in which a certain electronegative compound is to be measured in each, the attachment detection system will not be linearly calibrated unless the largest concentration produces a current decrease of not more than about ⅓ the carrier standing current at the test voltage. The deviation current ΔI in FIGS. 3*a* and 3*b* is, in fact, about ⅓ the current I_x and represents the largest concentration of that sample which can be measured linearly.

Optimum sensitivity and linearity are obtained when the current deviation at a sample peak of maximum concentration for the range to be tested is the maximum which can be obtained by variation of test conditions and is also just below ⅓ to ½ the standing current at the same conditions. FIGS. 3*a* and 3*b* also represent a maximum sensitivity operating condition to the extent that a higher or lower operating voltage would produce a lesser ΔI. Very often, however, the amount of sample gas is so small that there is no danger whatever that the deviation ΔI will approach ⅓ of the carrier standing current. In such cases—and the situation is by no means unusual—the goal is one of determining maximum sensitivity conditions in order to obtain a reliably high level of signal current for measurement.

The optimum represented by FIGS. 3*a* and 3*b* where maximum sensitivity and linearity limit coincide is more fortuitous than probable. Individual optimization of linearity and sensitivity is a more practical objective. Significantly, and in further accordance with the invention, it has been discovered that within the linearity restrictions sensitivity can be maximized or a large concentration range can be accommodated with sufficient sensitivity by varying diode spacing as well as varying the diode voltage in relating the attachment current deviation to the carrier standing current in the electron attachment mode of operation. The adjustable diode spacing provided by the apparatus previously described together with the maintenance of high resolution by reason of the sealed chamber volume which is also decreased with the spacing permits the operator to orient the operating points represented by particular voltages and particular spacings in terms of optimum available conditions for the particular sample and concentrations presented. The adjustment of the electrode spacing of a chamber in service, as distinguished from tests with different chambers having fixed electrodes, makes possible the quick and accurate determination of the best operating conditions with minimum reliance on indirect calibrations or data from earlier tests under possibly significantly differing details. Further, the spacing can be altered and test conditions reestablished not only for each group of samples to be compared, but also from sample to sample, or even from peak to peak within one sample separation.

The effect of diode spacing variation is illustrated by FIGS. 4*a* and 4*b*. As shown in FIG. 4*a*, the carrier (nitrogen) standing current always reaches the same current value plateau but requires successively higher voltages to do so as the spacing is increased. With a constant test proportion of an electronegative gas added to the carrier, the current decrease ($-\Delta I$) from the standing current reference level may be plotted against voltage to obtain the curve family of FIG. 4*b* at different diode spacings. This plot represents response to 1,4-dichlorobenzene; other electronegative materials tested have generally similar but not identical response curves. In each case the maximum response for a given spacing occurs at a voltage for which the carrier standing current is near or below the carrier standing current curve shoulder.

For establishing conditions of maximum sensitivity with a sample of given maximum concentration, the carrier gas plus the given sample concentration is passed through the detector cell under the same temperature, pressure, and flow conditions to be followed in subsequent testing. The FIG. 4*b* response curves are then run for a series of electrode spacings. The maximum signal deviation determines the optimum voltage and optimum spacing so far as sensitivity is concerned. Under the FIG. 4*b* conditions, the optimum spacing is 8 millimeters and the optimum diode voltage is about 10 volts. Unless the sample concentration is so high that the maximum response exceeds about ⅓ of the carrier standing current at the same voltage and spacing, no further calibration is required.

A short cut may be established for sample compounds which have been extensively tested. When the maximum response at each spacing, as shown in FIG. 4*b*, is less than approximately ⅓ of the standing current at the same voltage, as shown in FIG. 4*a*, the maximum response at each spacing is plotted against the spacing, as shown in FIG. 5. It will be found that, with tritium as the source of ionizing radiation, the response increases with spacing up to approximately 8 millimeters, beyond which the response usually remains constant at the same or a slightly lower value. The curve obtained in this manner is similar for different concentrations of the same compound and for different compounds, as long as the response is less than about ⅓ of standing current. Thus, by setting the diode spacing to approximately 8 millimeters and varying the voltage, the maximum sensitivity voltage operating point can be quickly found for many compounds.

When the condition for linearity is exceeded at maximum sensitivity, another method is employed. It will be appreciated from FIGS. 4*a* and 4*b* that decreasing the voltage from the optimum response value for a given spacing is unlikely to make the current response smaller than ⅓ or ½ of the standing current since the carrier standing current also decreases with decreasing voltage below the sample maximum response voltage for that spacing. Thus, referring to FIG. 4*b*, at an 8 millimeter spacing, the optimum response voltage is approximately 10. If the voltage is lowered, the response current drops, but so does the carrier standing current by nearly the same proportion. When the carrier standing current has been less than three times the optimum response at the optimum response voltage, decreasing the voltage has not been found helpful in appreciably increasing linearity for any of the compounds thus far tested.

The linearity solution lies in another direction. The voltage is maintained and the spacing is decreased. Thus, if the optimum responsive diode voltage of 10 at the spacing of 8 millimeters produces an optimum response greater than ⅓ of the carrier standing voltage, decreasing the spacing to 6 millimeters (or any spacing below 8 millimeters) reduces the sample response current at 10 volts (see FIG. 4*b*) and increases the carrier current at the same voltage (see FIG. 4*a*). The voltage may also be increased to further increase the sample concentration limit for which the current response increases linearly.

It will be appreciated that locating the voltages at which the current response is maximum for a number of spacings with the maximum concentration of the sample gas which is to be subsequently measured passing through the detector chamber is important. The operator thus derives, with the assistance of a few check points to determine the carrier standing current, sufficient information to optimize sensitivity and preserve linearity in establishing conditions for measuring the samples with the same adjustable electrode detector cell.

One precaution should be noted in increasing the voltage beyond the optimum response voltage. For many electronegative compounds, the deviation current not only decreases to zero but reverses in polarity and increases further. This effect varies for different compounds and the voltage at which the crossover (zero current deviation) occurs varies also with spacing. When sample components cannot be separated by the column, the detector spacing and voltage can sometimes be set at values corresponding to the crossover point for one of the components and at a reasonably high sensitivity for the others. The current response readings are thus for only the latter component despite the fact that the components are present at the same time in the detector chamber.

We claim as our invention:

1. An ionization detector cell for use in gas chromatography comprising a cylinder of insulating material, a perforated radioactive electrically conducting sheet covering one end of the cylinder, an electrically conducting piston having an end face parallel to said sheet in the cylinder, a gas-tight seal between the piston and the cylinder, means for adjusting the spacing of the piston from the sheet to provide an adjustable volume chamber, first means for introducing a chromatograph column effluent into said chamber, second means for passing the effluent from the chamber, said perforated sheet providing one of the first and second means, a passageway through the piston defining the other of said first and second means, said sheet constituting a cathode, and said piston constituting an anode for attachment in an external ionization measuring circuit.

2. An ionization detector cell for measurement of an electronegative gas component in a carrier gas subjected to ionization by measurement of the current decrease upon electron attachment to the electronegative gas molecules comprising a chamber having a uniform cross-sectional area along its axis, spaced parallel planar electrodes defining the respective inlet and outlet ends of the chamber, at least one opening in each of said electrodes for the passage of a gas stream therethrough, means for supplying a carrier gas stream at a constant flow rate to the chamber through the inlet electrode, a radiation source carried by one of said electrodes for providing ionizing radiation within the chamber, adjusting means connected to the other of said electrodes and extending externally from the chamber for adjusting the spacing of the electrodes from each other, a gas-tight seal between said other electrode and said chamber to prevent gas flow around said other electrode, the spacing range extending substantially above and below the average range of the beta particles from the radiation source through the chamber, means for placing the electrodes in the electrical circuit with the said other electrode at a positive steady-state potential with respect to the said one electrode, means included in circuit with said electrodes for measuring the ionization current collected, and means for adjusting said steady-state potential relative to the selected electrode spacing to control the current decrease upon electron attachment.

3. An ionization detection system for measurement of an electronegative gas component in a carrier gas subjected to ionization by measurement of the current decrease upon electron attachment to the electronegative gas molecules comprising a chamber having a uniform cross-sectional area along its axis, spaced parallel planar electrodes closing the respective ends of the chamber, at least one opening in each of said electrodes for the passage of a gas stream therethrough, means for supplying a carrier gas stream at a constant flow rate to the upstream end of the chamber, radioactive material carried by one of said electrodes for providing ionizing radiation within the chamber, adjusting means connected to the other of said electrodes and extending externally from the chamber for adjusting the spacing of the electrodes from each other, a gas-tight seal for preventing gas flow around said other electrode, the maximum spacing of said electrodes exceeding the average range of the radiating particles from said radioactive material, means for placing the electrodes in electrical circuit with the other electrode at a positive steady-state potential with respect to the one electrode, means included in circuit with said electrodes for measuring the ionization current collected, and means for adjusting said steady-state potential relative to the selected electrode spacing to control the current decrease upon electron attachment with a given concentration of a selected electronegative gas in the carrier gas to a value not in excess of one-third the ionization current of the carrier gas alone at the same electrode spacing and voltage.

4. The method of determining operating conditions for maximum sensitivity of an electron attachment detector for providing a current amplitude response varying with the amount of an electronegative gas carried in small proportions by a carrier gas stream flowing between an adjustably spaced pair of electrodes in the detection chamber

and subject to low-energy ionizing radiation, with a gas-tight seal between at least one of said electrodes to prevent gas flow around said electrode, which method comprises

first, adjusting the electrodes to a first trial spacing,

second, establishing the electronegative gas deviation current curve at that spacing with respect to voltage with the maximum concentration of the electronegative gas to be measured added to the carrier gas,

third, selecting the voltage for which the electronegative gas deviation current is maximum at the spacing,

fourth, repeating the foregoing steps at different spacings, and

fifth, selecting the spacing for which the maximum current is greatest and selecting the voltage producing that maximum current.

5. A method for establishing conditions to obtain linear response over an extended sample concentration range in the electron attachment mode of measuring the amount of electronegative gas component in a carrier gas stream passing between two spaced electrodes in an ionization chamber containing an ionization source, comprising the steps of, adjusting the electrode spacing to less than approximately the range of the ionizing particles radiating from said source and applying a direct voltage between the electrodes at an amplitude to provide at the maximum concentration a deviation current slightly less than approximately ⅓ of the carrier gas standing current for the same applied voltage at the same electrode spacing.

6. The method of claim 5 wherein said ionizing source is tritium and wherein as part of the first step electrode spacing is adjusted to less than approximately eight millimeters.

7. A method for eliminating interference between current responses to a plurality of gas sample components, at least one of said components exhibiting electron attachment, in a carrier gas stream passing between two electrodes in an ionization chamber which comprises, applying a low direct current potential between the electrodes, adjusting the spacing between electrodes, and varying the potential between the electrodes to minimize current response to at least one of said gas sample components.

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