

Description

The invention relates to a detector for a gas chromatograph comprising a heated emitter electrode; a heater source for energizing the emitter electrode; a nozzle disposed opposite to the emitter electrode; a sample gas flow route communicated to the nozzle; a carrier gas flow route communicated to the same nozzle; a collector electrode disposed in the proximity of the heated emitter electrode; an opposed electrode disposed opposite to the collector electrode; and a DC source connected to the collector electrode and the opposed electrode via an electrometer.

This detector is a device for detecting gases which were separated in a gas-chromatographic analysis.

In detecting presence of amine compounds and ammonia by a gas chromatographic analysis, conventionally applied were detectors of the type of thermal ionization or fluorescence in a post-column or colorimetry, all of these conventional methods are defective or unsatisfactory in terms of selectivity and sensitivity.

For instance, the thermal ionization detector is excellent in detecting nitrogen compounds, but this excellency is justified in the case of detecting all existing nitrogen compounds together and is not justified in selective detection of amine and ammonia compounds contained in other nitrogen compounds. Therefore, it is difficult by a thermal ionization detector to analyze only amine compounds. Further, this type lacks sensitivity of "ppb" order and inferior in repeatability, which leads to inadequacy to practical use and, additionally, the thermal ionization type always needs hydrogen gas, which will cause constant danger and demand close attention in analytical works. These are problems unsolved in conventional art.

Furthermore, a detector of the type mentioned in the beginning is described in the Journal of Analytical Chemistry of the USSR, Vol. 35, No. 6, Part 2, June 1980, pages 799-803, Plenum Publishing Corp., New York, US; E. Ya. Zandberg et al.: "High-sensitivity detector of amines and their derivatives". This detector has an ion emitter electrode made of oxidized molybdenum wire. However the work function of this emitter electrode material is relatively restricted, so that the ionization of amine compounds is not very easy.

Finally, in the Journal of Analytical Chemistry of the USSR, Vol. 38, No. 10, Part 1, October 1983, pages 1352-1356, Plenum Publishing Corp., New York, US; E.E. Sotnikov et al.: "Improved specificity and stability in a dual flame surface-ionization detector" there is described a flame surface ionization detector for the determination of compounds containing nitrogen, halogens, phosphorus and sulfur. As described in this publication the best electrode material for the negative surface-ionization electrodes was platinum, which gave stable results over a long period even at high concentrations. However, this known flame surface-ionization detector has another construction than the detector of the present invention.

According to a first aspect of the present invention there is provided a detector for a gas chromatograph of the type mentioned in the beginning which is characterized in that

(a) for the determination of amine compounds the emitter electrode (15) has at least part of its surface defined of metallic rhenium or iridium; or oxides of such metals; or a combination of such metals with such oxides; and

(b) a power controller (17) for maintaining the emitter electrode (15) at a temperature such that the emitter electrode (15) will ionize only amine compounds is provided.

According to a second aspect of the present invention there is provided a detector for a gas chromatograph of the type mentioned in the beginning which is characterized in that

(a) for the determination of amine compounds the emitter electrode (15) has at least part of its surface defined of metallic rhenium or iridium; or oxides of such metals; or a combination of such metals with such oxides;

(b) a power controller (17) for maintaining the emitter electrode (15) at a temperature such that the emitter electrode (15) will ionize only amine compounds is provided;

(c) a plurality of carrier gas flow routes (2) is provided; and

(d) means (19) for changing the polarity of the DC source (9) to change the detector (1) between surface ionization detecting mode and flame ionization detecting mode are provided.

Substantially, this invention proposes a detector device which is capable of serving as a surface ionization detector (hereinafter noted as SID) which is adapted to detect ions to be formed on the surface of a metal oxide compound having a large work function during in contact with amine compounds or ammonia and also serving as a flame ionization detector (hereinafter noted as FID) which has a popular or standard level of high-sensitivity for organic compounds or ammonia, wherein switch in the two alternative applications is made so ready.

Then, SID which is proposed by the present invention is based on the following principle:

When a gaseous sample of, for instance, amine compounds and oxygen-containing gas (for instance, air) are mixed and directed to contact with a heated solid surface (emitter) comprised of metallic rhenium or

iridium; or combination of such metals and oxides thereof, amine compounds and the like will heat-decompose on the surface to yield chemical species having lower ionization potentials and such chemical species are adapted to form surface ionization on the surface of a metallic emitter which is of a large work function and is also in thermal, electrical equilibrium with the chemical species. Measurement of ionizing current occurring such status will enable detection of amine compounds having lower work function, with outstanding selectivity and sensitivity. Herein, phenomenon of the surface ionization is explained by use of the following Saha-Langmuir's equation:

$$\frac{n_+}{n_0} = \frac{g_+}{g_0} \exp \left(- \frac{\Phi - IP}{KT} \right) \quad (1)$$

wherein n_+ / n_0 = a ratio of positive ions to neutral chemical species, Φ = work function on a metallic emitter at a temperature (T) of forming the surface ionization, K = Boltzmann constant, T = surface temperature of the metallic emitter, IP = ionization potential of the chemical species which are ionizing on the surface, g_+ / g_0 = the ratio of statistic weights of positive ions to the neutral chemical species. Following the formula above, at most cases, organic compounds tend to decompose on a heated metallic emitter surface to be chemical species having lower ionization potential than at original molecules and to be effectively ionized. Herein, ionic current ($i_s(T)$) by positive ions in connection with chemical species (S) which are formed on the metallic emitter surface is given below:

$$i_s(T) = nY_s(T) \cdot \beta_s(T) \quad (2)$$

wherein T = a temperature of the metallic emitter surface, $\beta_s(T)$ = ionization efficiency, n = number of organic molecules being impinged from gas phase on the surface, $Y_s(T)$ = a yield of chemical reactions on the metallic emitter surface. Further, $\beta_s(T)$ is denoted by the following formula with use of the Saha-Langmuir equation (1).

$$\beta_s(T) = \frac{1}{g_0 \exp \left(- \frac{\Phi - IP}{KT} \right) + g_+} \quad (3)$$

Review of the equations (2) and (3) leads to understanding that a metallic emitter which is disposed to arouse the surface ionization should have property of effecting heat-decomposition efficiently and have a larger work function, and that the surface ionization is specific to chemical species and is also strongly dependent on ionization potentials possessed by the chemical species.

Brief Description of Drawings

Fig. 1 is a schematic diagram showing an embodiment of the present invention. Figs. 2 and 3 are chromatograms indicating sensitivity and selectivity for amine compounds when a detector as shown in Fig. 1 is used as SID.

Best Mode for Carrying Out the Invention

The invention will be explained in the following with reference to the drawings.

Making reference to a detector 1 shown in Fig. 1, a carrier gas exit (outlet of a column) 2 is connected

with aid of a T-shaped joint 3 to a quartz-made nozzle 4 , and another pipe 5 to be connected to the T-shaped joint 3 is branched and it is connected through stop valves 5a , 5b to an oxygen or air source and a hydrogen source (these are not shown). An opening 6 of the nozzle 4 is opened in an ionizing chamber 7 and a nozzle electrode 8 is provided around the opening 6 and is in connection to DC source 9 with interposition of a polarity change switch 19 . The DC source 9 is generally adequate with a DC supply voltage of 200 to 300 V.

In neighborhood of the nozzle 4 in the ionizing chamber 7 , a pipe for oxygen or air supply 10 is provided. The oxygen or air is meant for maintaining space in the ionizing chamber 7 in oxidizing atmosphere wherefor the supply pipe 10 is preferably aided with provision of baffle plates to obtain uniform dispersion.

In opposing to the nozzle electrode 8 in the ionizing chamber 7 , a collector electrode 11 is provided, which is integrally formed with a cylindrical inner collector 12 and a cylindrical outer collector 13 with a ceramic-made insulating cylinder 14 interleaved wherein the outer collector 13 is extending cylindrically inwardly of the chamber to surround the heated emitter electrode 15 . The electrode 15 should be a wire, of which surface is covered with oxides of rhenium or iridium, wherein such oxides may be acceptable, if the oxides have been formed by heating prior to a target measurement. Further, the electrode 15 is connected with its one end to the edge of the inner collector 12 and with its the other end to the edge of the outer collector 13 , and further associated to a power controller 17 via a transformer 16 so that it may be heated to desired temperatures. Specifically noted, the electrode 15 is secured, for instance, at a position of ca. 6 mm apart from the nozzle electrode 8 . And one input terminal of the electrometer 18 is connected to secondary side of the transformer 16 which will reach the inner collector electrode 12 while the other terminal thereof is connected to the polarity change switch 19 . Based on arrangements as noted above, reference will be made to a case that the detector 1 is used as SID, for the first place.

Assuming that a sample gas (amine compounds and ammonia) flowing out of the exit 2 of the separation column is directed, upon open of the stop valve 5a , to mix at the T-shaped joint with air which is introduced by the pipe 5 . In this step, the flow rate of air is preferably 10 to 60 ml/min.

The sample gas mixed with air is flown into the ionizing chamber 7 by passing the edge of the nozzle 4 . The sample gas received in the ionizing chamber 7 is then mixed with air (20 to 100ml/min.) supplied from the pipe 10 and subjected to contact with the heated electrode 15 and then to decompose thermally whereby amine compounds and ammonia are ionized and yield positive ions.

In the step above, if the nozzle electrode 8 is applied with negative polarity of the DC source 9 by action of the polarity change switch 19 , the collector electrode 11 becomes positive whereby electrons yielded by cationization will be caught as electron current by the collector electrode 11 . This electron current is once detected by an electrometer 18 , it is amplified to be recorded by a recorder (not shown).

Results of measuring amine compounds and ammonia in those steps as noted above are demonstrated in chromatograms of Figs. 2 and 3, wherein the abscissa indicates time (min.) while the ordinate does voltage (100 scales define 0.01 volt). Analytical conditions involved are as follows:

A test sample used is 1.6 μ l of acetone solution containing 10 ppb of tri n-butyl amine and the column used is a glass column measuring 2.6 mm in inner diameter and 2 m in length, and packing material used is 80 to 100 mesh of Chromosord W covered with 15 % of Apiezon L and 5.0 % solution of potassium hydroxide. Temperature of the column is 150 °c and same of the detector is 250 °c. Range is $10^{10}\Omega$, full scale gives 0.02 volt and sensitivity is 2×10^{-12} A.

In Figs. 2 and 3, apparently appearing are peaks of tri n-butyl amine (denoted by A in Fig. 2 and by C in Fig. 3), wherein the peak A of tri n-butyl amine in Fig. 2 indicates 16 pg. and the peaks C in Fig. 3 does 160 pg of tri n-butyl amine while a peak D for n-dodecane indicates presence of 11.6 μ g of n-dodecane, which appearances show outstanding selectivity.

Next reference will be made to the detector device 1 applied as FID.

Assuming that a sample gas flowing out of exit of the separation column 2 , upon open of the stop valve 5b , is directed at the T-shaped joint 3 to mix with hydrogen introduced by the pipe 5 , wherein flow rate of hydrogen is preferably 40 to 80 ml/min.

The sample gas mixture with hydrogen is flown into the ionizing chamber 7 , wherein it is then mixed with air introduced by the pipe 10 to contact to the heated electrode 15 , whereby automatic firing takes place to give hydrogen flame at the opening 6 of the nozzle 4 .

At this moment, if the nozzle electrode 8 is applied with positive polarity of the DC source 9 by action of the polarity change switch 19 , the collector electrode 11 becomes negative. As result of combustion of organic compounds by hydrogen flame, positive ions are yielded containing carbon mostly and these ions are caught by the collector electrode 11 and are detected by the electrometer 18 . In steps now, the metallic compound of the electrode 15 acts as heating catalyst.

As described in the above, the detector device 1 is capable of two functions as SID and FID with ready switching operation.

Industrial Applicability

This invention enables analysis of ammonia, volatile amines etc that are controlled by the Bad Odor Prevention Act, by one analytical operation and further concentration is operationally convenience. Therefore, this invention will be applied to analysis of polluting compounds, for instance, ammonia and amine compounds present in water and further amine compounds present in living matters with high sensitivity wherein highly reliable analysis is performed with simple analytical operations as conventionally desired.

Claims

1. A detector (1) for a gas chromatograph comprising a heated emitter electrode (15); a heater source (16) for energizing the emitter electrode (15); a nozzle (4) disposed opposite to the emitter electrode (15); a sample gas flow route (2) communicated to the nozzle (4); a carrier gas flow route (2) communicated to the same nozzle (4); a collector electrode (11) disposed in the proximity of the heated emitter electrode (15); an opposed electrode (8) disposed opposite to the collector electrode (11); and a DC source (9) connected to the collector electrode (11) and the opposed electrode via an electrometer (18), characterized in that
 - (a) for the determination of amine compounds the emitter electrode (15) has at least part of its surface defined of metallic rhenium or iridium; or oxides of such metals; or a combination of such metals with such oxides; and
 - (b) a power controller (17) for maintaining the emitter electrode (15) at a temperature such that the emitter electrode (15) will ionize only amine compounds is provided.
2. A detector (1) for a gas chromatograph comprising a heated emitter electrode (15); a heater source (16) for energizing the emitter electrode (15); a nozzle (4) disposed opposite to the emitter electrode (15); a sample gas flow route (2) communicated to the nozzle (4); a carrier gas flow route (2) communicated to the same nozzle (4); a collector electrode (11) disposed in the proximity of the heated emitter electrode (15); an opposed electrode (8) disposed opposite to the collector electrode (11); and a DC source (9) connected to the collector electrode (11) and the opposed electrode via an electrometer (18), characterized in that
 - (a) for the determination of amine compounds the emitter electrode (15) has at least part of its surface defined of metallic rhenium or iridium; or oxides of such metals; or a combination of such metals with such oxides;
 - (b) a power controller (17) for maintaining the emitter electrode (15) at a temperature such that the emitter electrode (15) will ionize only amine compounds is provided;
 - (c) a plurality of carrier gas flow routes (2) is provided; and
 - (d) means (19) for changing the polarity of the DC source (9) to change the detector (1) between surface ionization detecting mode and flame ionization detecting mode are provided.

Revendications

1. Détecteur (1) pour chromatographe à gaz comprenant une électrode émettrice chauffée (15), une source de chauffage (16) pour l'alimentation en énergie de l'électrode émettrice (15), une buse (4) disposée à l'opposé de l'électrode émettrice (15) un chemin d'écoulement (2) pour l'échantillon gazeux communiquant avec la buse (4), un chemin d'écoulement (2) pour le gaz porteur communiquant avec la même buse (4), une électrode collectrice (11) disposée au voisinage de l'électrode émettrice chauffée (15), une électrode opposée (8) disposée à l'opposé de l'électrode collectrice (11), et une source de courant continu (9) raccordée à l'électrode collectrice (11) et à l'électrode opposée par un électromètre (18), caractérisé en ce que :
 - (a) pour la détermination des composés aminés, l'électrode émettrice (15) a une partie au moins de sa surface en rhénium ou iridium métallique, ou en oxydes de ces métaux, ou en une combinaison de ces métaux et de ces oxydes; et
 - (b) un contrôleur d'énergie (17) est fourni pour maintenir l'électrode émettrice (15) à une température telle que l'électrode émettrice (15) n'ionise que les composés aminés.

As described in the above, the detector device 1 is capable of two functions as SID and FID with ready switching operation.

Industrial Applicability

This invention enables analysis of ammonia, volatile amines etc that are controlled by the Bad Odor Prevention Act, by one analytical operation and further concentration is operationally convenience. Therefore, this invention will be applied to analysis of polluting compounds, for instance, ammonia and amine compounds present in water and further amine compounds present in living matters with high sensitivity wherein highly reliable analysis is performed with simple analytical operations as conventionally desired.

Claims

1. A detector (1) for a gas chromatograph comprising a heated emitter electrode (15); a heater source (16) for energizing the emitter electrode (15); a nozzle (4) disposed opposite to the emitter electrode (15); a sample gas flow route (2) communicated to the nozzle (4); a carrier gas flow route (2) communicated to the same nozzle (4); a collector electrode (11) disposed in the proximity of the heated emitter electrode (15); an opposed electrode (8) disposed opposite to the collector electrode (11); and a DC source (9) connected to the collector electrode (11) and the opposed electrode via an electrometer (18), characterized in that
 - (a) for the determination of amine compounds the emitter electrode (15) has at least part of its surface defined of metallic rhenium or iridium; or oxides of such metals; or a combination of such metals with such oxides; and
 - (b) a power controller (17) for maintaining the emitter electrode (15) at a temperature such that the emitter electrode (15) will ionize only amine compounds is provided.
2. A detector (1) for a gas chromatograph comprising a heated emitter electrode (15); a heater source (16) for energizing the emitter electrode (15); a nozzle (4) disposed opposite to the emitter electrode (15); a sample gas flow route (2) communicated to the nozzle (4); a carrier gas flow route (2) communicated to the same nozzle (4); a collector electrode (11) disposed in the proximity of the heated emitter electrode (15); an opposed electrode (8) disposed opposite to the collector electrode (11); and a DC source (9) connected to the collector electrode (11) and the opposed electrode via an electrometer (18), characterized in that
 - (a) for the determination of amine compounds the emitter electrode (15) has at least part of its surface defined of metallic rhenium or iridium; or oxides of such metals; or a combination of such metals with such oxides;
 - (b) a power controller (17) for maintaining the emitter electrode (15) at a temperature such that the emitter electrode (15) will ionize only amine compounds is provided;
 - (c) a plurality of carrier gas flow routes (2) is provided; and
 - (d) means (19) for changing the polarity of the DC source (9) to change the detector (1) between surface ionization detecting mode and flame ionization detecting mode are provided.

Revendications

1. Détecteur (1) pour chromatographe à gaz comprenant une électrode émettrice chauffée (15), une source de chauffage (16) pour l'alimentation en énergie de l'électrode émettrice (15), une buse (4) disposée à l'opposé de l'électrode émettrice (15) un chemin d'écoulement (2) pour l'échantillon gazeux communiquant avec la buse (4), un chemin d'écoulement (2) pour le gaz porteur communiquant avec la même buse (4), une électrode collectrice (11) disposée au voisinage de l'électrode émettrice chauffée (15), une électrode opposée (8) disposée à l'opposé de l'électrode collectrice (11), et une source de courant continu (9) raccordée à l'électrode collectrice (11) et à l'électrode opposée par un électromètre (18), caractérisé en ce que :
 - (a) pour la détermination des composés aminés, l'électrode émettrice (15) a une partie au moins de sa surface en rhénium ou iridium métallique, ou en oxydes de ces métaux, ou en une combinaison de ces métaux et de ces oxydes; et
 - (b) un contrôleur d'énergie (17) est fourni pour maintenir l'électrode émettrice (15) à une température telle que l'électrode émettrice (15) n'ionise que les composés aminés.



2. Détecteur (1) pour chromatographe à gaz comprenant une électrode émettrice chauffée (15), une source de chauffage (16) pour l'alimentation en énergie de l'électrode émettrice (15), une buse (4) disposée à l'opposé de l'électrode émettrice (15), un chemin d'écoulement (2) pour l'échantillon gazeux communiquant avec la buse (4), un chemin d'écoulement (2) pour le gaz porteur communiquant avec la même buse (4), une électrode collectrice (11) disposée au voisinage de l'électrode émettrice chauffée (15), une électrode opposée (8) disposée à l'opposé de l'électrode collectrice (11) et une source de courant continu (9) raccordée à l'électrode collectrice (11) et à l'électrode opposée par un électromètre (18), caractérisé en ce que :
- (a) pour la détermination des composés aminés, l'électrode émettrice (15) a une partie au moins de sa surface en rhénium ou iridium métallique, ou en oxydes de ces métaux, ou en une combinaison de ces métaux et de ces oxydes;
 - (b) un contrôleur d'énergie (17) est fourni pour maintenir l'électrode émettrice (15) à une température telle que l'électrode émettrice (15) n'ionise que les composés aminés;
 - (c) de nombreux chemins d'écoulement (2) pour le gaz porteur sont fournis; et
 - (d) des moyens (19) sont fournis pour changer la polarité de la source (9) de courant continu pour faire passer le détecteur (1) d'un mode de détection à ionisation de surface à un mode de détection à ionisation à la flamme.

Patentansprüche

1. Detektor (1) für einen Gaschromatographen, umfassend eine geheizte Emittierelektrode (15); eine Heizerquelle (16) für das Erregen der Emittierelektrode (15); eine gegenüber der Emittierelektrode (15) angeordnete Düse (4); einen Probengasströmungsweg (2), der in Verbindung mit der Düse (4) ist; einen Trägergasströmungsweg (2), der in Verbindung mit der gleichen Düse (4) ist; eine Kollektorelektrode (11), die in der Nähe der geheizten Emittierelektrode (15) angeordnet ist; eine gegenüberliegende Elektrode (8), die gegenüber der Kollektorelektrode (11) angeordnet ist; und eine Gleichstromquelle (9), die mit der Kollektorelektrode (11) und der gegenüberliegenden Elektrode über ein Elektrometer (18) verbunden ist, dadurch gekennzeichnet, daß
- (a) für die Bestimmung von Aminverbindungen bei der Emittierelektrode (15) wenigstens ein Teil ihrer Oberfläche aus metallischem Rhenium oder Iridium; oder Oxiden von solchen Metallen; oder einer Kombination solcher Metalle mit solchen Oxiden gebildet ist; und
 - (b) eine Leistungssteuer- bzw. -regeleinrichtung (17) zum Halten der Emittierelektrode (15) auf einer derartigen Temperatur, daß die Emittierelektrode (15) nur Aminverbindungen ionisiert, vorgesehen ist.
2. Detektor (1) für einen Gaschromatographen, umfassend eine geheizte Emittierelektrode (15); eine Heizerquelle (16) für das Erregen der Emittierelektrode (15); eine gegenüber der Emittierelektrode (15) angeordnete Düse (4); einen Probengasströmungsweg (2), der in Verbindung mit der Düse (4) ist; einen Trägergasströmungsweg (2), der in Verbindung mit der gleichen Düse (4) ist; eine Kollektorelektrode (11), die in der Nähe der geheizten Emittierelektrode (15) angeordnet ist; eine gegenüberliegende Elektrode (8), die gegenüber der Kollektorelektrode (11) angeordnet ist; und eine Gleichstromquelle (9), die mit der Kollektorelektrode (11) und der gegenüberliegenden Elektrode über ein Elektrometer (18) verbunden ist, dadurch gekennzeichnet, daß
- (a) für die Bestimmung von Aminverbindungen bei der Emittierelektrode (15) wenigstens ein Teil ihrer Oberfläche aus metallischem Rhenium oder Iridium; oder Oxiden von solchen Metallen; oder einer Kombination solcher Metalle mit solchen Oxiden gebildet ist; und
 - (b) eine Leistungssteuer- bzw. -regeleinrichtung (17) zum Halten der Emittierelektrode (15) auf einer derartigen Temperatur, daß die Emittierelektrode (15) nur Aminverbindungen ionisiert, vorgesehen ist;
 - (c) eine Mehrzahl von Trägergasströmungswegen (2) vorgesehen ist; und
 - (d) eine Einrichtung (19) zum Ändern der Polarität der Gleichstromquelle (9), um den Detektor (1) zwischen einer Oberflächenionisationsdetektionsbetriebsweise und einer Flammenionisationsdetektionsbetriebsweise zu ändern, vorgesehen ist.

