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(56) Documents Cited:
GB 2318874 A **GB 2305247 A**
US 20050092063 A1

(58) Field of Search:
UK CL (Edition X) **G1N**
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Other: **Online: WPI, EPODOC**

(54) Abstract Title: **An electrochemical gas sensor having two electrodes formed on a common support**

(57) An electrochemical gas sensor (10) for sensing two different toxic gases and having a housing (11) with at least one gas inlet (24) to allow gas to diffuse onto a electrode assembly (50) comprising two sensing electrodes (56,59) formed on a common support (61) with a gap(66) between the two electrodes, the gas passing through a filter housing (62) divided into separate compartments (68,69) for gas diffusion through each compartment to a respective selected electrode, one compartment (69) allowing the passage of unfiltered gas and the other compartment (58) containing a gas filter (81) to permit passage of a selected gas onto the respective electrode (59), the filter housing (62) also sealing against the support (61) in the gap (66) between the two electrodes.

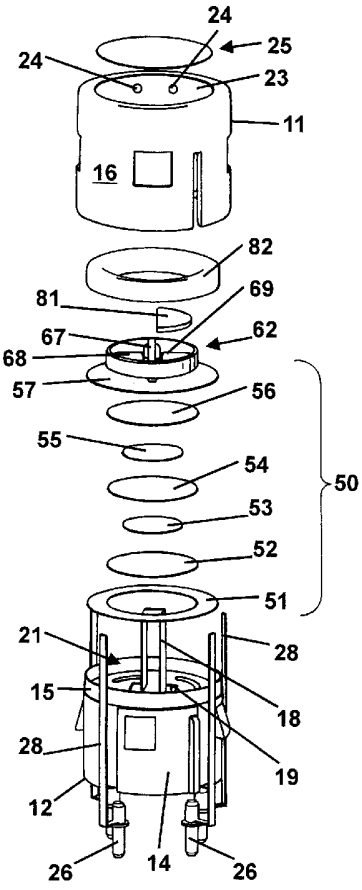

Fig. 3

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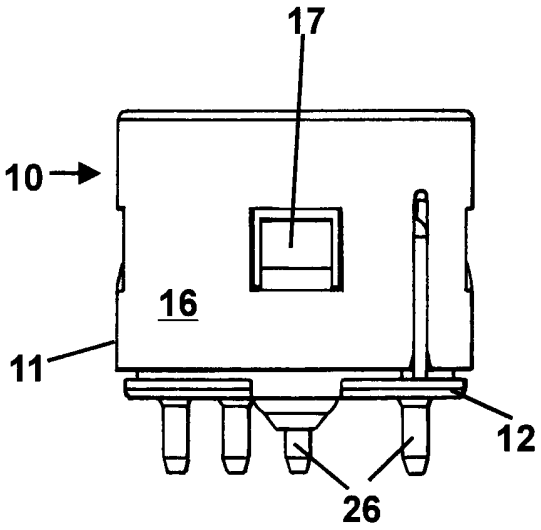

Fig. 1

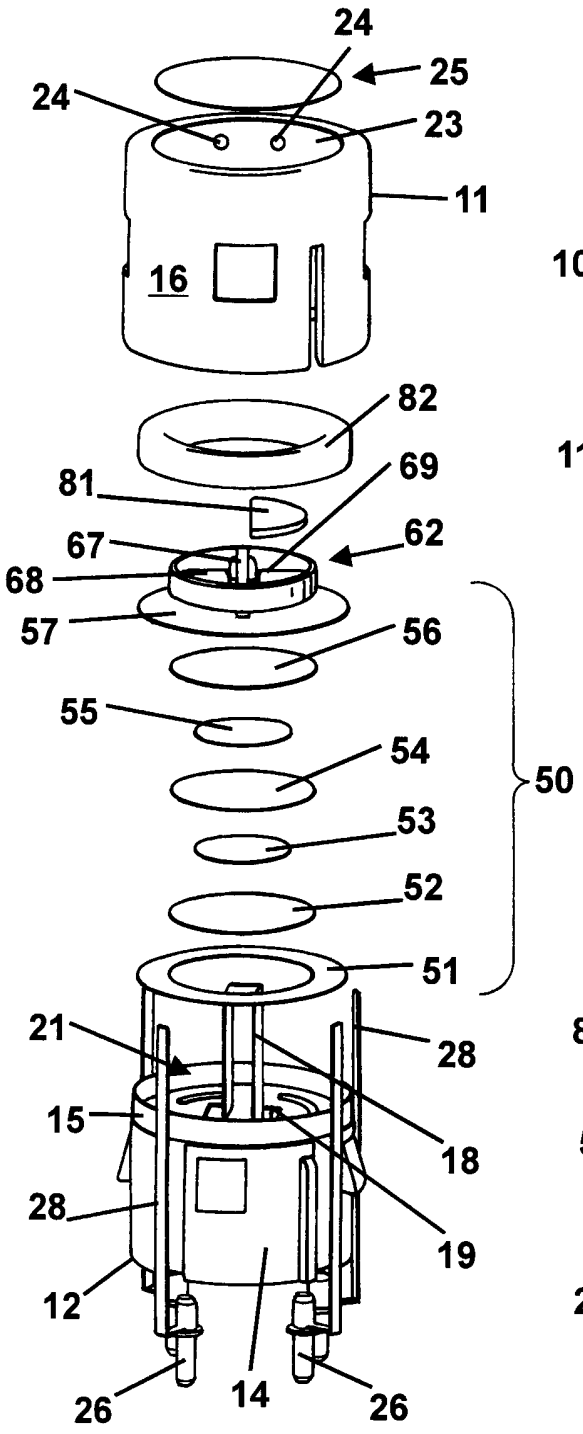

Fig. 3

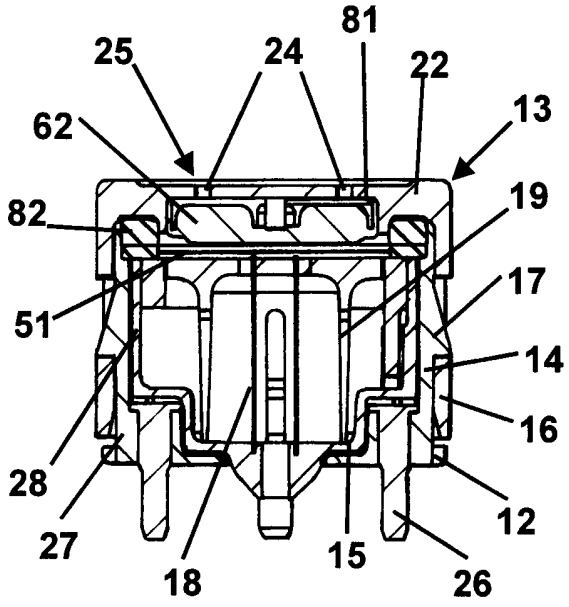

Fig. 2

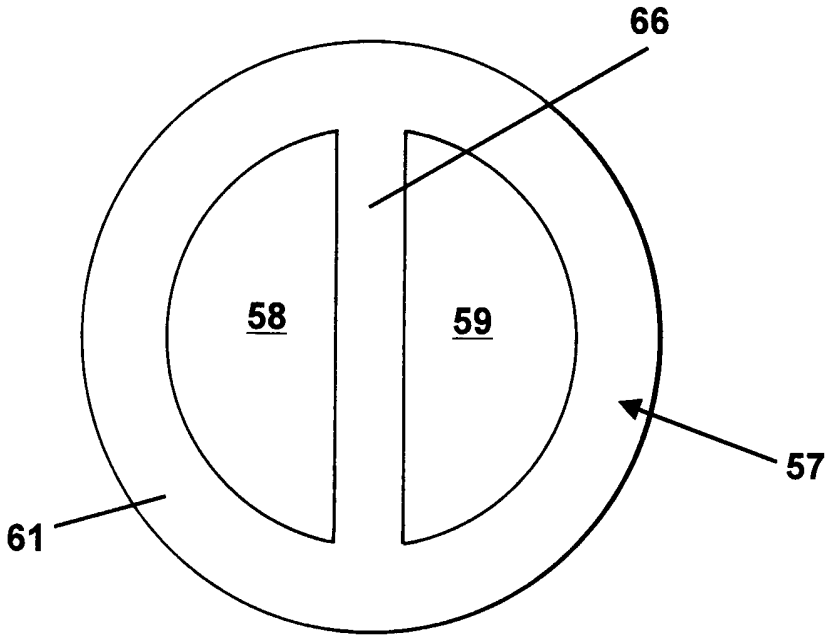

Fig. 4

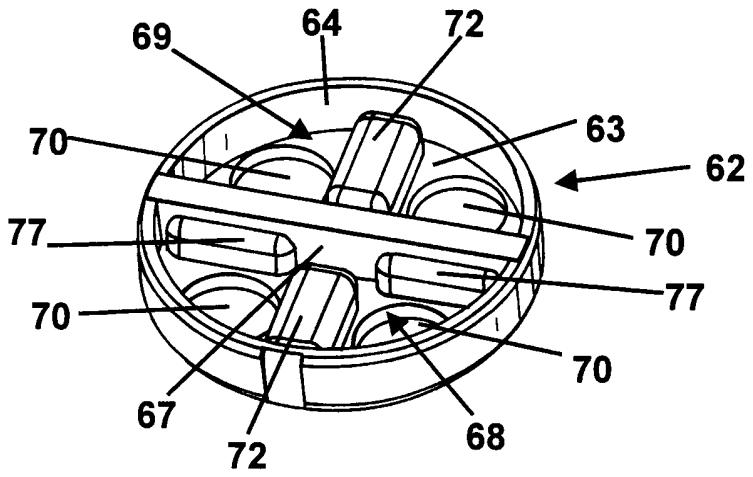

Fig. 5

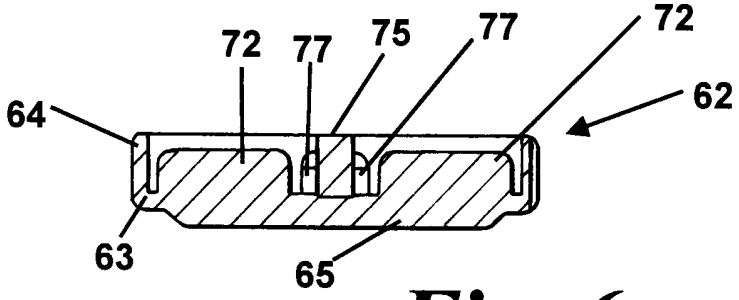

Fig. 6

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An Electrochemical Gas Sensor

Field

The present invention relates electrochemical gas sensors and in particular to gas sensors which may be utilised for independently detecting the presence of at least two different gases in a workplace atmosphere.

Background of the Invention

Small, portable, electrochemical gas sensors are well known and may be worn by personnel working in environments where toxic gases such as carbon monoxide and hydrogen sulphide may be present in the atmosphere. A known gas sensor is described in GB-A-2075197 which discloses a sensor used for sensing carbon dioxide gas. The general structure of the sensor shown in GB-A-2075 197 can be adapted for sensing other gases by the careful selection of materials used for the electrolyte, sensing electrode and counter electrode For example, GB-A-2371 873, there is disclosed a senor for detecting carbon monoxide which utilises electrodes having a platinum (Pt) black/PTFE catalytic layer on a PTFE support with a concentrated sulphuric acid electrolyte. It is also stated that such a detector is also suitable for sensing sulphur dioxide, hydrogen sulphide and nitric oxide.

Sensors for the detection of two or more gases are known from GB-A-2318 874 and EP-A-0994347 in which a plurality of different electrodes are utilised for the detection of different gases In GB 2318 874 the different electrode materials are located on one side of a diffusion membrane and cross-diffusion is reduced by gaps between adjacent electrodes, by selection of the electrode materials and by setting the potential of particular electrodes using a potentiostatic electrical system.

The present invention provides a simplified electrochemical sensor in which the cross diffusion and cross-sensitivity between different electrodes is ameliorated.

Statements of Invention

According to a first aspect of the present invention there is provided an electrochemical gas sensor having a sensor housing with at least one gas inlet allowing gas to diffuse through said inlet onto an electrode assembly comprising sensing electrodes formed on a common support with gap(s) between adjacent electrodes, the gas passing through a filter housing divided into separate compartments for gas diffusion through each compartment to a respective selected electrode, at least one compartment allowing the passage of unfiltered gas to a respective electrode and at least one other compartment containing a gas filter to permit a selected gas to diffuse to its respective electrode, with the filter housing also pressing against the support n to seal the gap between adjacent electrodes.

Preferably, the filter housing has base with a surrounding sidewall forming an open cavity divided into compartments by a partition, the base having apertures therein that connect each compartment with a respective electrode Preferably, a rib or ribs are provided on the underside of the base adjacent the support for pressing against the support and pressing the gap between electrodes onto the adjacent separator. The upper side of the base may be provided with raised bosses thereon to space the filter from the apertures formed in the base. Conveniently, the partition wall comprises a divider housed in a groove formed in raised rib on the base of the filter housing.

The sensor, preferably, has two sensing electrodes, one for the presence of one toxic gas and the other for sensing the presence of a second toxic gas.

The sensor may use platinum black and platinum black/ Ruthenium electrodes respectively and sulphuric acid electrolyte to sense the presence of carbon monoxide and hydrogen sulphide respectively. The electro potential difference generated by the different electrodes is measured directly with little or substantially no cross-sensitivity.

The sensor housing is a hollow cylindrical housing having top and bottom portions with overlapping sidewalls, the bottom portion including an electrolyte reservoir with a wick means providing a path for electrolyte from the reservoir to the electrodes, conductors connecting the electrodes to four pins set in the floor of the bottom portion, the conductors being accommodated between the sidewall of the bottom portion and the reservoir.

The top and bottom portions of the sensor housing are secured together by resilient clip means

According to a second aspect of the present invention there is provided a method of sensing two different toxic gases in which method the inwardly diffusing gases into a electrochemical gas sensor are divided into two separate gas streams and the two gas diffusion streams are directed to two spaced apart sensing electrodes formed on a single support with a gap therebetween, one of the gas streams being passed through a gas filter which allows a selected gas to diffuse to a selected electrode, with the other gas stream being directed to the other electrode without filtration, the two electrodes being sealed from each other and the potential difference due to the reaction at each electrode is independently measured.

The filtered gas stream may comprise CO which is directed onto a platinum black electrode, and the unfiltered gas stream is directed onto a platinum black/ruthenium electrode for the detection of H_2S

Description of the Drawings

The invention will be described by way of Example and with reference to the accompanying drawings in which :

Fig 1 is a side elevation of a assembled sensor according to the present invention,

Fig.2 is a vertical section through the sensor shown in Fig.1,

Fig 3 is an exploded isometric view of the components of the sensor shown in Fig 1,

Fig.4 is a view of the two sensitive electrodes and support,

Fig 5 is an isometric view of the filter housing , and

Fig 6 is a diametral cross-section through the filter housing

Detailed Description of the Invention

With reference to Figures 1 to 3, the sensor 10 comprises a generally cylindrical sensor housing or casing 11, made of a corrosion resistant engineering plastics material such as polycarbonate or polysulfone, approximately 20mm in diameter and 16mm in height. The sensor housing 11 is conveniently of two-part construction for assembly purposes and comprises a bottom portion 12 and a top portion 13 The bottom portion 12 has an upwardly extending sidewall 14 forming an internal cavity in which is housed an electrolyte reservoir 15 also made of polysulfone or polycarbonate. The top portion 13 has a downwardly

extending sidewall 16 which fits over the bottom portion sidewall 15 and the two portions are held together by resilient clips 17

The electrolyte reservoir 15 is provided with a wick 18 of unbound glass fibre, which constitutes hydrophilic non-conductive electrolyte wicking material, extending into the reservoir for contact with electrolyte therein. The wick 18 is held in a support 19 moulded from a suitable plastics material such as polyethylene. The top surface of the reservoir 15 has a circular recess 21 with an annular shoulder which is use receives an electrode stack 50

The top portion 13 has a top wall 22 with a circular recess 23 therein with openings 24 therein to permit gas passage to the interior of the housing 11. The openings 24 are covered on the outer side by a dust cover 25 which is porous to gases.

The bottom portion 12 of the housing 11 supports four connector pins 26 each of which extends through the bottom wall 27 of the housing and is connected on its inner end to a conductor strip 28 The conductor strips 28 extend upwardly between the inner surface of the sidewall 14 and the reservoir 15 and in use connect with electrodes as will be explained later

The electrode stack 50 is best seen in Figure 3 The components of the electrode stack 50 are generally of planar or sheet like configuration. The stack 50 has an annular floor seal 51 made from PTFE polymer material and which sits on the shoulder in the recess 21 of the reservoir 15 This is followed by a circular separator disc 52 made of unbound glass fibre which constitutes a hydrophilic, non-conductive material permeable to the electrolyte and

that functions as electrolyte-wicking material The end portion of one conductor strip 28 is then folded across the separator disc 52 and functions as an electrical conductor for connection to a first terminal pin 26 on the sensor housing The assembly then includes a circular counter electrode 53 The counter electrode 53 comprises a catalytic layer covering the full extent of one face of a gas porous PTFE support. The stack 50 then includes a second separator disc 54 similar to separator disc 52 followed by is circular reference electrode 55 of similar materials and construction to the counter electrode 53 . Then follows a conductor strip 28 leading to a second terminal pin 26. A third separator disc 56 similar to discs 52,54 is then provided, followed by an portions of third and fourth conductor strips 28, as previously described and leading to a third and fourth terminal pins

The electrode stack 50 further comprises a circular electrode assembly 57 shown in detail in Figure 4 and comprising two substantially semi- circular sensing electrodes 56,59 on a gas porous PTFE support 61. One sensing electrode 58, in use for sensing Carbon monoxide comprises platinum black/PTFE catalytic layer on the microporous PTFE support 61 and the other sensing 59, in use sensing hydrogen sulphide, comprise a platinum black/ ruthenium mix /PTFE catalytic layer on the PTFE support . The catalytic layer is formed from a mixture of catalyst material and PTFE binder, printed onto the support, subject to pressure and sintered at elevated temperature to give a porous binder/catalyst layer bonded to the support The electrode assembly 57 is orientated with the catalytic layers face downwards and connecting with respective conductor strips.

A disc-like filter housing 62 is located on top of the electrode assembly 57. The housing 62 is shown in Figures 6 & 7 and is circular having a base 63 with an upstanding sidewall 64 surrounding the base 63 The underside of the base 63, adjacent the electrode assembly

57, has at least one diametral rib 65 thereon which in use presses against the PTFE support 57 , which in turn seals the gap 66 between the adjacent electrodes 58,59 on the underside of the support 57 against the separator 56 In an alternative arrangement, a pair of ribs mutually intersecting ribs extending normally or each other may be provided.

The upper portion of the filter housing 62 has an open cavity divided into two semi circular compartments 68, 69 by a diametral partition wall 67. The partition wall 67 may be moulded integrally with the base 63 or alternatively may comprise a divider 75 located in a groove formed in two aligned radial ribs 77. Each compartment 68,69 has at least one aperture 70, and in this example two apertures, in its base which permits gas to pass through the base 63 to the respective electrodes 58 ,59 At least one compartment 69, and preferably both compartments, is provided with a raised boss 72 formed on the base 63 The boss 72 and raised ribs 77 provide a support for a semi-circular filter 81 spaced from the aperture 70 in the base of the respective compartment 69.

An "O" ring 82 is located on top of the assembly, being sized to contact the outer sidewall 64 of the filter housing and the outer margin of the PTFE support 61 On insertion of the assembly into the housing 11, as shown in Figure 1, the top wall 22 contacts the "O" ring 82 which urges the electrode assembly 57 into contact with the outer periphery of the floor seal 51 forming a seal, also bringing the various electrode stack components into close contact as shown The top wall 22 presses against the divider 75 of the filter housing 62 and against the top of the sidewall 64 urging the housing 62 against the electrode assembly 57. During this assembly some of the electrode stack components deform from their initially planar condition

Concentrated sulphuric acid electrolyte is located in the chamber within reservoir 14 for contact with wick 18 The reservoir is not filled completely with electrolyte, leaving a free volume in the reservoir to allow for the possibility of water absorption resulting in an increase in the electrolyte volume.

The electrode supports and floor seal 51 are all made from hydrophobic microporous PTFE. The hydrophobic properties of the material mean it is impermeable to the electrolyte so that electrolyte is effectively sealed within the housing by virtue of the floor seal 51 and the electrode assembly support 61 and the "O" ring 82

The geometry of the various components of the electrode stack is selected so that the separator discs 52,54,56 are of greater extent than the reference and counter electrodes. This means that protruding portions of the separator discs are urged into contact so that these components also act as wick means providing a path for electrolyte to pass by capillary action from the reservoir to all the planar electrodes, thus providing electrolytic continuity between the electrodes

When the sensor is assembled the divider 75 seals one opening 24 from the other opening 24 and effectively divides the inward diffusion of gases into two streams. One stream of gas passes through the filter 81 which permits the passage on CO gas only, the other stream of gas passes through the filter housing unfiltered. The filtered gas stream then reacts with the electrode 58 and the other unfiltered stream of gas reacts with the electrode 59

The rib 65 on the base 63 of the filter housing 62 is pressed against the PTFE support 57 in alignment with the gap 66, pressing the support against the separator 56 sealing the

electrodes from each other This is sufficient to prevent cross contamination between the two electrodes

In use, the sensor is exposed to a gas sample, possibly containing carbon monoxide, and hydrogen sulphide to be measured and which gains access to the electrodes of the sensor via opening 24 The casing terminal pins 26 are connected to an external electronic apparatus , which is used to sense the potential differences of the sensing electrodes 58,59 with respect to the potential of the reference electrode 55.

The chemical reactions between the Carbon Monoxide gas, and hydrogen sulphide gas and the respective electrodes 58,59 are well known and do not form a part of the present invention.

The illustrated sensor is thus a compact, robust, sealed unit that can be used in any orientation and which can sense two gases with little or no cross-contamination and does not require the use of a complicated potentiostatic system

Claims

1 An electrochemical gas sensor having a sensor housing with at least one gas inlet allowing gas to diffuse through said inlet onto a electrode assembly comprising sensing electrodes formed on a common support with gap(s) between adjacent electrodes, the gas passing through a filter housing divided into separate compartments for gas diffusion through each compartment to a respective selected electrode, at least one compartment allowing the passage of unfiltered gas to a respective electrode and at least one other compartment containing a gas filter to permit a selected gas to diffuse to the respective electrode, with filter housing also sealing against the support in the gap between adjacent electrodes

2 A sensor as claimed in Claim 1, wherein the filter housing has base with a surrounding sidewall forming an open cavity divided into compartments by a partition wall, the base having apertures therein that connect each compartment with a respective electrode

3 A sensor as claimed in Claim 2 wherein ribs are provided on the underside of the base adjacent the support in use pressing the electrode assembly support between the electrodes against an adjacent separator

4 A sensor as claimed in Claim 2 or Claim 3, wherein the partition wall comprises a divider housed in a groove formed in raised rib on the base of the filter housing.

5 A sensor as claimed in any one of Claims 1 to 4 and which has two sensing electrodes, one for the presence of one toxic gas and the other for sensing the presence of a second toxic gas

6. A sensor as claimed in Claim 5 and which uses platinum black and platinum black/ Rubidium electrodes with sulphuric acid electrolyte to sense the presence of carbon monoxide and hydrogen sulphide respectively

7. A sensor as claimed in Claim 5 or Claim 6, wherein the sensor housing is a hollow cylindrical housing having top and bottom portions with overlapping sidewalls, the bottom portion including an electrolyte reservoir with a wick means providing a path for electrolyte from the reservoir to the electrodes, conductors connecting the electrodes to four pins set in the floor of the bottom portion, the conductors being accommodated between the sidewall of the bottom portion and the reservoir

8. A sensor as claimed in Claim 7, wherein the top and bottom portions of the sensor housing are secured together by resilient clip means.

9 A method of sensing two different toxic gases using an electrochemical sensor in which method the inwardly diffusing gases into the sensor are divided into two separate gas streams and the two gas diffusion streams are directed to two spaced apart sensing electrodes formed on a single support with a gap therebetween, one of the gas streams being passed through a gas filter which allows a selected gas to diffuse to a selected electrode, with the other gas stream being directed to the other electrode without filtration, the two electrodes are sealed from each other and the potential difference due to the reaction at each electrode is independently measured.

10. A method as claimed in Claim 9, wherein the filtered gas stream comprises CO which is directed onto a platinum black electrode, and the unfiltered gas stream is directed onto a platinum black/ruthenium electrode for the detection of H_2S, and the electrolyte comprises sulphuric acid

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Application No: GB0605193.2 **Examiner:** Eamonn Quirk

Claims searched: 1-10 **Date of search:** 28 June 2006

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
X,Y	X:1, 9, 10 Y:2 at least	US2005/092063 A1 (Riken Keiki KK) figures, Sesnor SC, filter 60B, sensor SB.
Y	2 at least	GB2305247 A (Draegerwerk AG) see figures, electodes 8,12,13
Y	2 at least	GB2318874 A (Draegerwerk AG) see figures electrodes 4,5,13, and filter 13

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category	P	Document published on or after the declared priority date but before the filing date of this invention
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^{X} :

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Worldwide search of patent documents classified in the following areas of the IPC

G01N

The following online and other databases have been used in the preparation of this search report

Online: WPI, EPODOC