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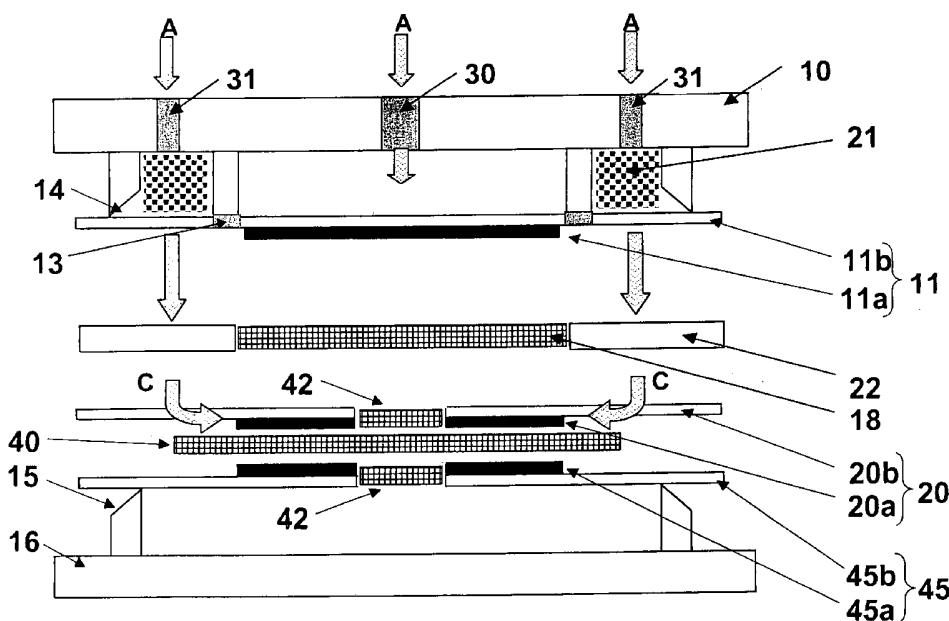
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(54) Title: ELECTROCHEMICAL GAS SENSOR



(57) Abstract: An electrochemical gas sensor for detecting at least one gas species present in an atmosphere. The gas sensor comprises: a first gas sensing electrode (16) adapted to detect at least a first target gas species; a first gas path (30) for guiding the gas to the first gas sensing electrode; a second gas sensing electrode (20) adapted to detect at least a second target gas species, the first and second gas sensing electrodes being located on opposite sides of an electrolyte-containing region; a second gas path (31) between the atmosphere and the second electrode, the gas path bypassing the first gas sensing electrode; and a counter electrode (45).

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ELECTROCHEMICAL GAS SENSOR

This invention relates to an electrochemical gas sensing device, particularly suited to the independent
5 detection of at least two gas species in an atmosphere.

Electrochemical sensors for the detection of toxic gases are widely used in a variety of safety critical applications, especially in industrial environments. They are usually based on gas diffusion electrodes in contact
10 with liquid electrolyte which is typically immobilised in wicks and separators. Such electrodes conventionally allow facile gas diffusion within their structures since they comprise a mixture of noble metal catalyst and hydrophobic phase pressed onto a porous hydrophobic support. Sensors
15 based on such principles are described for example in GB 2094005 and represent a long life and robust solution to the demand for accurate concentration measurement of a single trace gas at reasonable cost.

Frequently, several such devices are deployed in
20 portable instruments to provide a multi-gas capability, often combined with sensors based on other technologies (for example, catalytic detectors for the measurement of combustible species). However, manufacturers of such instruments continually strive to reduce their size and
25 weight for the benefit of users whilst simultaneously increasing the functionality of the units. The demand for smaller sensors is driven by the desire to make instruments more ergonomic and cheaper for the user. Smaller sensors mean that thinner, more lightweight instrument housings can
30 be employed. This in turn means that the instrument can be more readily carried by the user, thus providing improved personal protection in a range of environments. Alternatively, the reduced size can be utilised to increase the number of sensors in existing instruments thereby
35 increasing their functionality without any increase in size. For this reason, there is a strong desire to miniaturize the sensors, and reduce their power consumption

(so limiting the battery capacity required) whilst not compromising the performance of the sensor. In this respect, it is important that the sensing electrode size is maintained as the size of the overall sensor is reduced.

5 One approach addressing this issue is to design electrochemical sensing elements which are capable of providing measurements of more than one gaseous species with the required degree of specificity, rather than needing two separate elements to achieve the same result.
10 For example, carbon monoxide and hydrogen sulphide are frequently present in hazardous areas and conventionally two separate sensing devices and associated processing channels are required to measure them. However, both gases will react with reasonable activity on certain
15 electrocatalysts, so that a single sensing electrode might, in principle, be used to measure both species. In practice, the situation represents a difficult problem for the sensor designer since it is not possible to identify which species is causing the response or whether a mixture
20 of species is present. In circumstances where different alarm limits are required for each gas, or they have significantly different reactivities with the electrode, this is clearly unacceptable.

One method of overcoming this problem is to sweep the
25 bias voltage applied to a sensing electrode and then to analyse the response to determine which species are present and at what concentrations. Such voltammetric techniques are well known in analytical science and are powerful tools, capable of differentiating between different species
30 such as carbon monoxide and hydrogen sulphide. However, the complexity of the operating and interrogation systems required prevents their widespread adoption in relatively low-cost instrumentation for use in rugged industrial environments.

35 Another method for the specific detection of multiple analytes within a single sensor adopts a complementary approach and exploits the widely differing reactivities of

gases on some electrocatalysts. By employing this effect in combination with an understanding of the gas diffusion processes within the sensor, the measurement of two or more species on multiple sensing electrodes within a single device is feasible. This provides considerable cost savings over the use of two individual sensors since the sensor casing, electrolyte, gas diffusion barrier, counter and reference electrodes may be shared, making it possible to design smaller instruments offering at least the same degree of functionality.

One commercial product which uses such an approach to detect hydrogen sulphide and carbon monoxide is the 4COSH CiTiceL® by City Technology Limited, illustrated schematically in Figure 1 of the accompanying drawings. The gas, of composition A, enters the sensor through the diffusion barrier 1 which in this case is a capillary aperture. The gas encounters a first sensing electrode, comprising an electrocatalyst 3 mounted on a backing tape 2. Gas is able to diffuse through the sensing electrode arrangement. A separator 4, wetted with electrolyte, contacts the catalyst 3 which is selected to provide significantly greater reactivity towards hydrogen sulphide than carbon monoxide. The electrode operates in a standard potentiostatic circuit with a reference and a counter electrode, not shown, to output a reliable measure of the hydrogen sulphide concentration. Unreacted gas components, including carbon monoxide, then diffuse radially through the electrode backing tape where contact is made with backing tape 6 of the second sensing electrode. The gas reaching the second catalyst area 5 has a composition B, with a much lower concentration of hydrogen sulphide than the initial composition A. Catalyst 5 is optimised to provide good reactivity towards carbon monoxide and therefore provides a measurement of the carbon monoxide concentration in the ambient gas. Direct diffusion of gas from the first catalyst 3 to the second catalyst 5 is prevented by the presence of the wetted separator, which

also increases the probability of the hydrogen sulphide reaction on catalyst 3 being completed before the species can diffuse onto the second sensing electrode.

Although this design works well, there are a number of potential problems which can lead to operational difficulties. It is possible to make the first sensing electrode highly specific to hydrogen sulphide such that interference by carbon monoxide present in the atmosphere is minimal. In contrast however, hydrogen sulphide will react more vigorously than carbon monoxide even on electrocatalysts notionally optimised for the detection of the latter. Therefore, unreacted hydrogen sulphide reaching the second sensing electrode can cause measurement errors. Furthermore, the extent of any such hydrogen sulphide transmission is likely to vary due to changes in the ambient conditions. For example, at high temperatures and low humidity, the separator 4 may begin to dry out. This can reduce the efficiency of the reaction taking place on the electrocatalysts and may also allow more hydrogen sulphide to reach the second electrocatalyst 5. It is therefore difficult to accurately compensate for the hydrogen sulphide contribution ("cross sensitivity") to the reaction occurring on electrocatalyst 5 in its output signal.

Figure 2 shows an example of this behaviour, plotting the hydrogen sulphide cross sensitivity measured on the second sensing electrode as a function of time for two sensors maintained at different humidities. Sensor (i) was maintained at 0% relative humidity, whereas sensor (ii) remained in conditions of ambient humidity. It may clearly be seen that the degree of hydrogen sulphide transmission and hence cross sensitivity increases rapidly as a function of time in dry conditions.

An alternative sensor arrangement is disclosed in US 5,865,973 (Kiesele et al) in which 3 sensing electrodes are arranged side by side. By providing each gas sensing electrode with a separate gas access route, it is possible

to condition the gas incident on each electrode independently. However, the arrangement disclosed in US'973 is inefficient in its use of space and requires a very large sensor envelope to accommodate all the sensing electrodes in such a way that they each have access to the ambient gas. The resulting sensor footprint is extensive. To reduce the size of this sensor, the electrode area itself would have to be reduced, which has a number of undesirable consequences. In the absence of any other differences, the catalyst loading defines the electrode activity. This in turn defines the ability of the electrode to consume all of the gas presented to it via the diffusion barrier, a condition required to allow direct correlation of signal to external gas concentration. It is well known that low activity catalysts therefore cope less well with higher target concentrations and generally perform more poorly.

Similarly, a highly active electrode has a greater "activity reserve" i.e. improved ability to continue operating as intended even in the event of some activity loss through, for example, poisoning.

The same catalyst loading can in principle be applied to a smaller footprint by making the electrode thicker. But this increases the demands upon the diffusibility of the structure if catalyst at the base is to present similar activity to that near the surface. In practice, thick catalyst layers offer poorer performance than thinner, wider layers having the same loading.

If the reductions in catalyst loading are essential (e.g. to create side by side assemblies) then the fundamental electrode signal for a given gas concentration will be smaller under diffusion limited operation. This in turn means that the lowest detectable gas concentration will increase, compromising the operation of the sensor as a trace detector. Therefore, it would be advantageous to maintain the sensing electrode area whilst reducing the overall size of the sensor.

DE-C-4041143 describes an electrochemical gas sensor which can detect several gases simultaneously. It comprises a sensing electrode and a counter electrode and the gaseous pollutants are not individually detected but
5 instead an electric signal is produced corresponding to the proportions of the gaseous pollutants detected.

In contrast, EP-A-1154267 describes a sensor in which the inventors seek to make a specific measurement of a single target gas. Thus, the intention of the system
10 described is to minimize the cross-sensitivity to a coexisting species. In the example described, it is intended to overcome the interference on a CO sensor due to hydrogen, whether the gas coexists in the atmosphere or is generated inside the cell by electrochemical action. Two
15 methods for achieving this compensation are described. The first is essentially a transient approach, which relies on "current dumping" by the sensing electrode in response to the hydrogen-induced shift in reference potential. Appropriate design of the electrode can tune this current
20 flow to provide some degree of cancellation of the hydrogen signal generated by gas on the sensing electrode. However, this is unsuitable for applications where long term gas exposures may occur. The alternative is to provide two reference electrodes in the sensor, one of which undergoes
25 potential shift in response to hydrogen as above, and one which is sufficiently well buried within the sensor structure to avoid any significant hydrogen-induced effect. By measuring the difference in potential between these otherwise identical electrodes, a compensating signal may
30 be derived.

In accordance with the present invention, an electrochemical gas sensor for detecting a plurality of gas species present in an atmosphere comprises a first gas sensing electrode adapted to detect at least a first gas
35 species; a first gas path for guiding the gas to the first gas sensing electrode; a second gas sensing electrode adapted to detect at least a second gas species, the first

and second gas sensing electrodes being located on opposite sides of an electrolyte-containing region; a second gas path between the atmosphere and the second electrode, the gas path bypassing the first gas sensing electrode and having a filter disposed therein, the filter preventing substantially any interfering gas species from reaching the second electrode; and a counter electrode.

In this context, an "interfering species" refers to any gas species which may react significantly on the second gas sensing electrode, other than the target gas species which the second sensing electrode is adapted to detect. A gas sensor as above described allows at least two gas species to be individually and reliably measured by a single sensor unit using two or more sensing electrodes. The measurements obtained from this sensor are much less prone to variation as the sensor ages or experiences different ambient conditions than sensors which operate on the previously described principle of sequential electrode reactions. The invention ensures that the second gas sensing electrode does not primarily rely on the transmission of unreacted gas from the first gas sensing electrode in order to provide its output signal. Instead, the sensor provides parallel routes for the gas to reach the gas sensing electrodes within the sensor. By locating the gas sensing electrodes on opposite sides of the electrolyte-containing region and arranging the gas path to the second gas sensing electrode such that it bypasses the first gas sensing electrode, it is possible to place the electrodes above one another. This significantly reduces the lateral area required by the sensing electrodes and makes it possible to minimise the footprint area of the sensor without reducing the size of each electrode. By maintaining the electrode area, the performance of the electrode is not compromised and the sensor is able to detect trace gas concentrations.

The stacked sensor structure created by positioning the electrodes on opposite sides of the electrolyte has a number of further advantages.

5 Firstly, an assembly which has multiple sensing electrodes side by side (such as US'973) will need to be built into the sensor in a particular orientation, for example to ensure that the different electrodes align with the required gas inlet channel. Stacking circular electrodes as proposed in the present invention reduces the risk of errors during assembly of the sensor.

10 Secondly, side-by-side electrodes would be printed onto a single substrate. Printing multiple (different) catalysts onto the same substrate is a difficult process. It is generally not possible or desirable to cure the electrodes more than once, which means that, in a side-by-side sensor, all electrodes must be subjected to the same treatment. However, different catalyst formulations adapted for the detection of different gas species may actually benefit from rather different treatment regimes.

15 Again, this is much more readily accommodated during sensor production if the sensing electrodes are on separate substrates.

The gas sensing electrodes may be metal foils, meshes or compressed powder tablets. Preferably, however, the first and second gas sensing electrodes each comprise a sensing electrocatalyst mounted on a gas permeable tape. Conveniently, the electrolyte-containing region comprises a separator wetted with electrolyte although it would be possible to use a volume of liquid electrolyte which is not immobilised in separator or other similar material. Such a "free" liquid electrolyte acts as an effective diffusion barrier but is prone to a number of performance problems such as orientation sensitivity. Other types of electrolyte might include solid ion conductors (e.g. beta alumina) and polymer electrolytes (e.g. Nafion). If a liquid-soaked separator is used, the gas sensor may further comprise an electrolyte reservoir which supplies

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electrolyte to the separator via a wick. Preferably, the separator is restrained by a gas porous washer which forms part of the second gas path. This ensures that the wetted separator is concentrically centred within the sensor stack and hence aligns with the electrodes as intended. This arrangement helps to ensure that gas reacting at the first gas sensing electrode does not reach the second gas sensing electrode whilst minding that the passage of gas through the gas path to the second gas sensing electrode is not hindered by the electrolyte containing region.

Generally, the electrochemical gas sensor further comprises a housing. For ease of construction, the housing may comprise two parts, the first part providing the base of the sensor and the second part providing the top of the sensor. Alternatively the housing could be made as a single piece or in several pieces. A single-piece design would, however, require that the electrodes are in-situ before the moulding or forming process takes place. Whilst theoretically possible, this is a difficult process in practice. If a powder filter is used, instead of or in addition to cloth filters, it is preferable to form the top of the sensor from two pieces which inter-engage to retain the filter in the top of the sensor, although a single-piece construction is also possible.

Although the sensing electrodes could each be supplied with gas via a common diffusion barrier, it is preferable that the first gas path communicates with the atmosphere via a first gas diffusion barrier and the second gas path communicates with the atmosphere via a second gas diffusion barrier.

By providing the gas sensor with separate gas diffusion barriers for each gas sensing electrode, it is possible to tune the gas diffusion barrier in each pathway to control the rate of gas access to each electrode independently. This can be used to provide appropriate scaling for the electrode output in view of the anticipated concentration of each target species. It is therefore

preferable that the first and second gas diffusion barriers are each adapted to limit the transport of the atmosphere to each gas sensing electrode in accordance with the properties of the gas sensing electrode and/or of the target gas species. The first and second gas diffusion barriers may comprise gas phase diffusion barriers such as capillary apertures or Knudsen barriers. Alternatively, they could comprise solid diffusion barriers.

In the case of capillaries, preferably the capillary apertures of the first gas diffusion barrier and the capillary apertures of the second gas diffusion barrier are of different dimensions. For example, gas that is expected to be present in high concentrations can be measured in a channel having a relatively restrictive gas diffusion barrier and therefore be prevented from overloading the electrode. The use of small gas access apertures can also provide a significant improvement to the operational life of any inboard filter material. It is preferable for the filter to be disposed inboard of the second diffusion barrier.

It would be possible to arrange the sensor such that gas enters the two gas paths on opposite sides of the sensor. However, it is preferable that the entrance to the first and the entrance to the second gas paths are located in the top of the sensor, the second gas path guiding the gas past the first gas sensing electrode. This achieves a more compact sensor arrangement and enables one side of the sensor to be mounted onto a surface without obstructing gas entry. Furthermore, by having all gas accesses to the sensor located in close proximity, the gas feed arrangements within instruments may be simplified. Only a small part of the sensor needs to be exposed to the atmosphere, which can be an important consideration as instruments shrink and the available surface area on cases reduces. If feeding gas to the sensor in a pumped system, there are similar simplifications by co-locating the apertures.

The counter electrode may conveniently be a counter/reference electrode capable of acting both as a counter electrode and a reference electrode, each gas sensing electrode operating in two-electrode mode in conjunction with the counter/reference electrode. In order to reduce costs, one common counter/reference electrode could be used in conjunction with each of the gas sensing electrodes. However, if so desired, multiple counter/reference electrodes may be employed. For example, the gas sensor may further comprise an additional counter/reference electrode for each gas sensing electrode.

Alternatively, the gas sensor may further comprise a reference electrode, each gas sensing electrode operating in three-electrode mode in conjunction with the counter and reference electrodes. Again, multiple counters and/or reference electrodes may be employed.

Preferably, the sensor further comprises a sensing circuit coupled with the sensing electrodes. Each gas sensing electrode may be held at a bias voltage, thereby improving the specificity of the reactions occurring thereon. By changing the operating potential of the electrode, the same electrode can be used to detect a different target gas species. For example, what may be an interfering gas species when the electrode is operated at one potential may become the target gas species at a different operational bias. This may be achieved using appropriate biasing methods which may be different for each electrode. Alternatively, the bias voltage could be swept across a range of voltages or zero bias could be applied.

An example of an electrochemical gas sensor in accordance with the present invention will now be described and contrasted with a known sensor with reference to the accompanying drawings, in which:-

Figure 1 is a schematic cross-section of an electrochemical gas sensor which operates according to known principles;

Figure 2 is a graph indicating the hydrogen sulphide cross sensitivity as a function of time occurring in an electrochemical gas sensor as shown in Figure 1;

Figure 3 is a schematic cross-section of an example of an electrochemical gas sensor which illustrates the principles of the invention;

Figure 4 shows an exploded perspective view of a first portion of an example of an electrochemical gas sensor according to the invention;

Figure 5 shows an exploded perspective view of a first embodiment of a second portion of the electrochemical gas sensor shown in Figure 4;

Figure 6 shows an exploded underneath perspective view of the second portion of the electrochemical gas sensor as shown in Figure 5;

Figure 7 is a graph indicating the hydrogen sulphide cross sensitivity as a function of time measured in an electrochemical gas sensor as depicted in Figure 3;

Figure 8 shows an exploded view of a second embodiment of a second portion of the electrochemical gas sensor shown in Figure 4;

Figure 9 shows an exploded underneath perspective view of the second portion of the electrochemical gas sensor as illustrated in Figure 8; and

Figure 10 is a circuit diagram illustrating an example of a sensing circuit which may be used in conjunction with an electrochemical sensor of the type shown in Figure 3.

The electrochemical gas sensor illustrated schematically in Figure 3 comprises a sensor top provided with a central gas diffusion barrier and a second gas diffusion barrier comprising one or more additional gas access points towards the sensor perimeter. Ambient gas, of composition A, enters the sensor through diffusion barriers and 31. A first gas sensing electrocatalyst 11a is mounted on a backing tape 11b which is sealed to the sensor top at region 13. Together, the first sensing electrocatalyst 11a and the

backing tape 11b form the first gas sensing electrode 11. A second gas sensing electrode 20 is disposed on the opposite side of a separator 18. The second gas sensing electrode 20 consists of a sensing electrocatalyst 20a mounted on a backing tape 20b. The electrocatalysts 11a and 20a may be chosen from a range of precious metal catalysts, alloys and mixtures such as platinum, gold, ruthenium and graphite in various combinations. The backing tapes 11b and 20b must be formed from gas porous materials such as PTFE. By positioning the gas sensing elements 11 and 20 on opposite sides of the separator 18, it is possible to reduce the size of the sensor footprint for a given electrode area.

The tapes 11b and 20b are sealed between mating chamfered edges 14 and 15 of the sensor top 10 and sensor base 16 on final assembly. This together with the seal at region 13, effectively creates two gas paths within the sensor body; one from the gas diffusion barrier access point 30 to the first gas sensing electrode 11, and a peripheral path accessed by one or more gas access points 31 towards the outer edges of the sensor top 10. This peripheral path bypasses the first electrode and is conveniently an annular volume although different physical shapes of path and arrangements of gas diffusion barriers may be used to suit the preferred sensor layout.

Gas in the first path reacts on the first gas sensing electrode 11 in which the electrocatalyst 11a is selected to detect a first target species with high specificity. It is important that the backing tape 11b must not allow any significant radial gas movement across regions 13 or 14.

In the case of region 14, any radial transfer potentially compromises the composition of the gas passing from aperture 31 to electrode 20. This effect may be irrelevant if the ambient gas is identical at the side of the sensor to that at the front face - but this may not necessarily be the case. Such "side leakage" is not normally considered a beneficial feature (other than when

there is the need to ensure especially good oxygen access to a counter, e.g. for high concentration sensors).

Electrocatalyst 11a extends to meet region 13 at the perimeter of the inner sealed region, thereby preventing
5 unreacted gas transmission around the side of the catalyst into the second gas chamber. Gas is constrained to diffuse vertically through the sensor, which has important consequences for the behaviour of the device. A number of
10 methods for creating these seals may be employed, but conveniently an annular heat stake can be used in the case of region 13, and tape compression between annular sealing faces 14 and 15. Mechanical compression provides an effective long-term seal against electrolyte leakage. Both
15 methods have the effect of increasing the lateral diffusion resistance of the normally porous backing tape 11b to an extent where it becomes large compared with that offered by the orthogonal face.

The separator 18 is connected to a wick and electrolyte reservoir, which are not shown in Figure 3, and
20 thereby remains saturated with electrolyte. The wetted separator 18 permits only low rates of gas transfer and acts as a relatively effective gas diffusion barrier. This, and the greatly restricted radial diffusion route
25 through tape 11b means that gas entering through the central gas diffusion barrier 30 is held in the vicinity of catalyst 11a. This results in more complete reaction of the target species on the catalyst 11a than might otherwise be the case. The transport of potentially interfering
30 species from the first gas path to the second gas path is substantially eliminated. Furthermore, the output from the first sensing electrode 11 is much less prone to variations due to target species diffusing around the catalyst rather than being brought into contact with it.

Separator 18 is conveniently chosen to have a diameter
35 at least as large as, and often slightly bigger than, catalyst region 11a so that all of the catalyst effectively contributes to the electrochemical reaction. Separator

misalignment can result in poor catalyst wetting. However, the separator 18 cannot be made to occupy the full width of the sensor body, since this would disrupt the gas flow through the peripheral regions of the backing tapes 11b and 20b. The electrochemical gas sensor shown in Figure 3 solves this problem by incorporating an additional component to restrain the separator 18. Gas porous washer 22 laterally surrounds the separator 18 and ensures that it remains centrally located in the assembly. This further improves the consistency of wetting of electrode 11, allowing proper utilisation of the full electrode diameter, and producing more predictable and reliable gas diffusion behaviour within the sensor. Washer 22 is typically made from the same porous materials as the electrode backing tapes 11b and 20b, and therefore offers similarly facile gas transmission. Suitable materials for this application include the polymeric material PTFE.

The gas entering the sensor at diffusion barrier 31 (also of initial composition A) reaches the second gas sensing electrode 20 via a gas path which bypasses catalyst 11a. A filter 21 is disposed in the gas path so that gas species which may interfere with the detection of the second target gas species are trapped, absorbed or consumed by the filter 21. The resulting gas, of composition C, contains effectively no interfering gas species and passes through backing tapes 11b and 20b to reach catalyst 20a. Catalyst 20a is selected to detect a second target gas species. The interference of the output signal, produced by unwanted species reaching catalyst 20a, is limited by the selectivity of the electrochemical reaction occurring thereon, but is further enhanced by the performance of the filter material 21.

In Figure 3, the arrangement is shown as a two-gas system where catalyst 20a and tape 20b are in an annular form where the central aperture allows the electrolyte wick to pass through from the reservoir and reach separator 18. However, it will be apparent that with suitable design

modifications, the second gas sensing electrode 20 could in fact take the form of two or more separate components or sectors, each connected by an independent filtered gas path to the surrounding atmosphere. The principles used in the electrochemical gas sensor shown can be extended to beyond two target gas species if desired. Filter materials could also be incorporated in between gas diffusion barrier 30 and first gas sensing electrode 11 in order to further improve the specificity of the signal obtained from the first gas sensing electrode 11.

A further advantage of the electrochemical gas sensor arrangement shown in Figure 3 is that it is possible to tune the diffusion properties of gas diffusion barriers 30 and 31 to suit the required sensitivity and range of each gas sensing electrode according to well-known principles. This is in contrast to the situation previously encountered and shown in Figure 1 where a compromise capillary dimension must be used. Thus, gases expected to be present in high concentrations can be measured in a channel having a relatively restricted gas diffusion barrier and therefore be prevented from overloading the gas sensing electrode. The use of small gas access apertures can also provide significant improvements in the operational life of the inboard filter material.

Generally, only one counter and one reference electrode would be used in conjunction with the two or more gas sensing electrodes in order to reduce costs. However, multiple counters and/or references may be employed if so desired. For example, the use of a different reference electrode in each circuit might allow a more favourable sensing electrode potential to be maintained without the need for any external bias voltage to be supplied from the potentiometric circuit. It should also be noted that although the description here has concentrated on systems employing a separate counter electrode and reference electrode ("three-electrode mode"), it would be possible to

use a single electrode to act as both the counter and reference electrodes ("two-electrode mode").

The example shown in Figure 3 has a single counter/reference electrode 45. Like the gas sensing electrodes 11 and 20, the counter /reference electrode 45 comprises a catalyst layer 45a and a backing tape 45b, again made from a gas porous material such as PTFE. A further separator layer 40 is disposed between counter/reference electrode 45 and the second gas sensing electrode 20, and wicking components 42 (which may also be made of separator material) are provided to supply both separators 18 and 40 with electrolyte.

The gas sensing electrodes are connected, along with the counter and reference electrodes, to a sensing circuit such as that shown in Figure 10. This is a typical potentiostatic operating circuit based on amplifier IC1 and is intended for use in conjunction with a combined CO and H₂S sensor, in which case the electrodes are unbiased. Components IC2 and IC3 are amplifiers which act as current to voltage converters, thereby producing an easily handled voltage output from the current generated at the relevant sensing electrodes. Transistors J177 ensure that the sensing electrodes are shorted to the reference when IC1 is switched off, thereby providing repaired start-up.

Figure 4 shows an exploded assembly drawing of a combined carbon monoxide and hydrogen sulphide electrochemical sensor which uses the principles described above with reference to Figure 3. The sensor is conventionally assembled from the bottom up so that the stack of components can be directly located into a cylindrical housing 60. The housing 60 is usually made from injection moulded plastic and is provided with connection pins 61, one for each electrode. The pins 61 are in turn spot welded to current collectors 59 which are shown folded back to allow access to the housing base, but which are bent over into position as the stack is assembled. In this case, the current collectors 59 are

made from platinum ribbons. Beneath the stack of components, there is an electrolyte reservoir not visible in Figure 4.

Counter electrode 58, which includes a layer of catalyst, is inserted first with the catalyst facing upwards. This is followed by a wicking component 57 and the counter current collector is then folded in, followed by separator 56, a second current collector 59 and the reference electrode 55, with its catalyst facing downwards. Separator 54 and a third current collector 59 follow. The second gas sensing electrode 53, which corresponds to the second gas sensing electrode 20 shown in Figure 3, is placed in the stack with its platinum catalyst facing downwards. A porous washer 52, separator 51, fourth current collector 59 and first gas sensing electrode 50 complete the stack of components. Electrode 50 corresponds to the first gas sensing electrode 11 of Figure 3 and is positioned with its catalyst facing downwards. In practice, the first gas sensing electrode 50 is usually heat sealed to the sensor top before final assembly as will be described below. The first gas sensing electrode 50 employs a platinum/ruthenium alloy catalyst which provides minimal cross sensitivity to carbon monoxide, typically less than 2%.

Figure 5 shows the upper parts of the electrochemical gas sensor assembly, comprising a sensor top 71 which mates with the base 60 after completion of the stack assembly and may be sealed to it using one of a number of methods, for example ultrasonic welding. In this example, the gas diffusion barrier which enables the first gas sensing electrode 50 to communicate with the atmosphere comprises a central capillary aperture 72 having a diameter of 2.3mm. The second gas diffusion barrier, through which gas reaches the second gas sensing element 53 comprises three smaller capillaries 73, each 0.7mm in diameter and arranged around the perimeter of the sensor top 71. The capillaries 72 and 73 are covered by a gas porous self-adhesive membrane 70

which performs the dual functions of preventing significant ingress of dust and particles which might block the capillaries and limiting the bulk flow of gas through the apertures which would otherwise interfere with the diffusion control of the capillary barriers and can cause signal errors.

Figure 6 illustrates the sensor top assembly from below and clearly depicts how central capillary 72 provides access to chamber 75 whereas peripheral capillary 73 allows gas into the annular region 76. In the example shown, two annular filters 74 made from silver-impregnated carbon cloth material (Charcoal Cloth Company) are located in chamber 76 and oxidise virtually all hydrogen sulphide present so that the hydrogen sulphide cross sensitivity on the second gas sensing electrode 58 is less than 0.5%. The first gas sensing electrode 50 is heat sealed to the flat surface of the wall which divides chambers 75 and 76 before final assembly thereby creating the sealed areas which correspond to region 13 in Figure 3.

The completed sensor envelope conforms to a typical industry standard, having a diameter of 20.4mm and a body height of 16.6mm. Connection to the external potentiostatic circuitry is via four contact pins 61, each 1.5mm in diameter, which protrude 4.3mm from the base of the sensor.

Figure 7 illustrates the performance of a sensor built in the manner described but with a Purafil (potassium permanganate on alumina) powder filter in chamber 76 to remove hydrogen sulphide. Region (i) indicates 0% relative humidity, and (ii) ambient relative humidity. The hydrogen sulphide cross interference signal is significantly lower than the values obtained with the known design shown in Figure 2. Furthermore, there is comparatively little drift following an initial settling period, even though continued operation at 0% relative humidity could have a detrimental effect upon the wetting of separator 51 and hence the activity of the first sensing electrode. The design

improvements offered by an electrochemical sensor as described above clearly produce a sensor with much more reliable and robust two-gas performance under such demanding conditions.

5 Although the sensor arrangement shown in Figures 4 to 6 does allow the use of filters in powder form, it is better suited to the use of cloth material such as filter components 74. Difficulties arise because after filling with powder, the single-piece sensor top 71 must be
10 inverted to allow joining to the base. However, the outer perimeter of the powder-filled chamber 76 is not sealed until the top and bottom chamfers are brought together, and therefore some powder spillage is possible.

 Figures 8 and 9 illustrate a two-piece top design
15 which is better suited to the use of powder filters. In this case, the base and stack assembly is constructed as shown in Figure 4 and described above. Using the two-piece arrangement, the first gas sensing electrode 50 is heat sealed to annular face 92 on top 88 and this is welded to
20 base 60 around the chamfered surface 91. Having thus closed the stack and base assembly, the sensor may be stood the correct way up to complete the top. If required, powder filter material may be placed in the recesses 92 formed between radial arms 91 in top 88. The arms help to
25 distribute the powder and retain it in position over the life of the sensor. Alternatively or additionally, annular filters 87 may be placed in the positions shown.

 Component 86 is a gas porous disk, typically made from PTFE, which is provided with an annular self-adhesive
30 region 85 allowing it to be attached to the underside of cap 81, and a central aperture 95. Disk 86 provides retention of filter powder, if used, once the top assembly has been completed. The diameter of aperture 95 is greater than that of capillary 82, but small enough that the outer
35 capillaries 83 are covered by the PTFE and hence that the filter material in the outer channels is properly retained. The aperture diameter is chosen to be slightly larger than

that of the raised feature 89 so that a seal may be formed between raised feature 89 and the underside of cap 81. This prevents cross talk between the two gas paths.

Alternatively, disk 86 could be a whole disk (not shown), without an aperture. In this case, compression of the disk 86 against the underside of cap 81 by raised feature 89 when the top assembly is completed would provide an annular seal whose radial diffusion resistance is large compared with the vertical resistance through the membrane face. This would effectively seal the gas access route to the first gas sensing electrode 50 from the gas path which leads to the second gas sensing electrode 53. In practice, it has been found that when the disc is used without an aperture, there is actually a greater degree of cross talk between the two gas streams. An annular heat seal to cap 81 could alternatively be used to provide the separation between the two gas access routes.

The required membrane compression and filter retention is obtained by snap fitting cap 81 into the central recess provided in top 88. Matching features 84 on the cap locate with matching ridges in apertures 92 and retain the cap in position. Bulk flow membrane 80 is fitted over cap 81 and performs the same roles as membrane 70, previously described.

A further advantage of this arrangement is that it is possible for the two sets of diffusion barrier capillary access holes, 82 and 83, to be located more closely together on the sensor top 81 than is the case with the example shown in Figures 5 and 6. This can offer advantages when incorporating the sensor into instrument designs where the available gas access area is limited. In both sensor design examples, all capillaries are assumed to be exposed to the same ambient gas, although the two sets could be fed by different gas streams if the application so demanded. The greatest demands are however placed upon the performance of the electrochemical sensor when a single gas stream is presented at the front face of the device and in

this situation, the advantages of the sensor arrangement disclosed herein are most apparent.

The same sensor arrangement has another potential application. By making an appropriate choice of first and second gas sensing electrodes, filters and gas diffusion barriers, the two gas paths can be used to monitor the same gas species but at two different concentration levels within the same sensor. For example, a highly active electrode fed by a large capillary (or alternative diffusion barrier allowing a large amount of gas to enter the gas path) could be used to give trace gas measurements. A much smaller capillary (or alternative), feeding to a second gas sensitive electrode, could provide measurements at higher concentrations. The second gas sensing electrode could also be designed to be less active than the first sensing electrode, in order to increase the gas concentration level it can measure. The lower activity could be achieved by using a lower surface area form of the same catalyst as the first gas sensing electrode, by using a different catalyst, by operating the electrode as a different bias voltage or by a combination of one or more of these methods.

In such an arrangement, a filter 21 such as that shown in Figure 3 may be disposed in both the first gas path and the second gas path, since the same target gas species should reach each gas sensing electrode. Alternatively, if there are no interfering species present, the sensor arrangement shown in Figure 3 could be used without any filter material.

In operation in an atmosphere of increasing target gas concentration, the output of the high sensitivity channel (large capillary gas path) would first be monitored. Then, at a preset output level, attention would switch to the low sensitivity channel. As the concentration of the target gas species in the ambient gas falls, the two channels would be monitored in reverse order. To optimise this approach, it is advantageous to provide each gas sensing

electrode with its own counter electrode since a very high gas concentration may overload the current demands on the counter electrode linked to the high sensitivity gas sensing channel.

5 Such a gas sensing device would be useful in a range of environments, especially those in which there are different levels of risks associated with low and high concentrations of the target gas species in the atmosphere. For example, some gases are both toxic and flammable:
10 carbon monoxide, ammonia and hydrogen sulphide all present such risks. A gas sensing device as described above could comprise a first channel, having a large capillary, able to detect ppm-level gas concentrations, to monitor for toxic exposure hazards. A second channel, with a much more
15 restricted capillary, could measure the gas in the percent range, at which level the gas may be liable to combust in air.

CLAIMS

1. An electrochemical gas sensor for detecting at least
5 one gas species present in an atmosphere, the gas sensor
comprising:
 a first gas sensing electrode adapted to detect at
 least a first target gas species;
 a first gas path for guiding the gas to the first gas
10 sensing electrode;
 a second gas sensing electrode adapted to detect at
 least a second target gas species, the first and second gas
 sensing electrodes being located on opposite sides of an
 electrolyte-containing region;
15 a second gas path between the atmosphere and the
 second electrode, the gas path bypassing the first gas
 sensing electrode; and
 a counter electrode.
2. An electrochemical gas sensor according to claim 1
20 wherein the first and second gas species are different gas
species.
3. An electrochemical gas sensor according to claim 1
wherein the first and second gas species are the same gas
species.
- 25 4. An electrochemical gas sensor according to any one of
the preceding claims which further comprises a filter
disposed within the first gas path, the filter
substantially preventing any interfering gas species from
reaching the first gas sensing electrode.
- 30 5. An electrochemical gas sensor according to any one of
the preceding claims which further comprises a filter
disposed within the second gas path, the filter
substantially preventing any interfering gas species from
reaching the second gas sensing electrode.
- 35 6. An electrochemical gas sensor according to claim 5
when dependent on claim 2.

7. An electrochemical gas sensor according to claim 5 when dependent on claims 3 and 4.
8. An electrochemical gas sensor according to claim 7 wherein the first gas sensing electrode and the second gas sensing electrode are of different activities.
9. An electrochemical gas sensor according to any one of the preceding claims wherein the first gas path communicates with the atmosphere via a first gas diffusion barrier and the second gas path communicates with the atmosphere via a second gas diffusion barrier.
10. An electrochemical gas sensor according to claim 9 when dependent on claim 5 wherein the filter is disposed inboard of the second gas diffusion barrier.
11. An electrochemical gas sensor according to claim 9 or claim 10 wherein the first and second gas diffusion barriers are each adapted to limit the transport of the atmosphere to each gas sensing electrode in accordance with the properties of the gas sensing electrode and/or of the target gas species.
12. An electrochemical gas sensor according to claim 11 wherein the first and second gas diffusion barriers are each adapted to limit the transport of the atmosphere to each gas sensing electrode in accordance with a desired concentration range of the target gas species.
13. An electrochemical gas sensor according to claim 12 when dependent on claim 7 or claim 8.
14. An electrochemical gas sensor according to any of claims 9 to 13 wherein the first and second gas diffusion barriers comprise capillary apertures.
15. An electrochemical gas sensor according to claim 14 wherein the capillary apertures of the first gas diffusion barrier and the capillary apertures of the second gas diffusion barrier are of different dimensions.
16. An electrochemical gas sensor according to any one of the preceding claims wherein the first and second gas sensing electrodes each comprise a sensing electrocatalyst mounted on a gas permeable tape.

17. An electrochemical gas sensor according to any one of the preceding claims wherein the electrolyte-containing region comprises a separator wetted with electrolyte.
18. An electrochemical gas sensor according to claim 17
5 which further comprises an electrolyte reservoir which supplies electrolyte to the separator via a wick.
19. An electrochemical gas sensor according to claim 17 or claim 16 wherein the separator is restrained by a gas porous washer, wherein the washer forms part of the second
10 gas path.
20. An electrochemical gas sensor according to any one of the preceding claims which further comprises a housing.
21. An electrochemical gas sensor according to claim 20 wherein the housing comprises two parts, the first part
15 providing the base of the sensor and the second part providing the top of the sensor.
22. An electrochemical gas sensor according to claim 21 wherein the top of the sensor is formed from two pieces which inter-engage to retain the filter in the top of the
20 sensor.
23. An electrochemical gas sensor according to any one of the preceding claims wherein the entrance to the first and the entrance to the second gas paths are located at the top of the sensor, the second gas path guiding the gas past the
25 first gas sensing electrode.
24. An electrochemical gas sensor according to any of the preceding claims wherein the counter electrode is a counter/reference electrode, capable of acting as both a counter electrode and a reference electrode, each gas
30 sensing electrode operating in two-electrode mode in conjunction with the counter/reference electrode.
25. An electrochemical gas sensor according to claim 24 which further comprises an additional counter/reference electrode for each gas sensing electrode.
- 35 26. An electrochemical gas sensor according to any of claims 1 to 23 which further comprises a reference electrode, each gas sensing electrode operating in

three-electrode mode in conjunction with the counter and reference electrodes.

27. An electrochemical gas sensor according to claim 26 wherein a counter electrode is provided for each gas sensing electrode.
5

28. An electrochemical gas sensor according to claim 26 or claim 27 wherein a reference electrode is provided for each gas sensing electrode.

29. An electrochemical gas sensor according to any of the preceding claims further comprising a sensing circuit coupled with the sensing electrodes, wherein each gas sensing electrode is held at a bias voltage.
10

30. An electrochemical gas sensor according to at least claim 2 adapted to individually detect hydrogen sulphide and carbon monoxide present in the atmosphere.
15

31. An electrochemical gas sensor according to claim 30 wherein the first gas sensing electrode is adapted to detect hydrogen sulphide and the second gas sensing electrode is adapted to detect carbon monoxide.

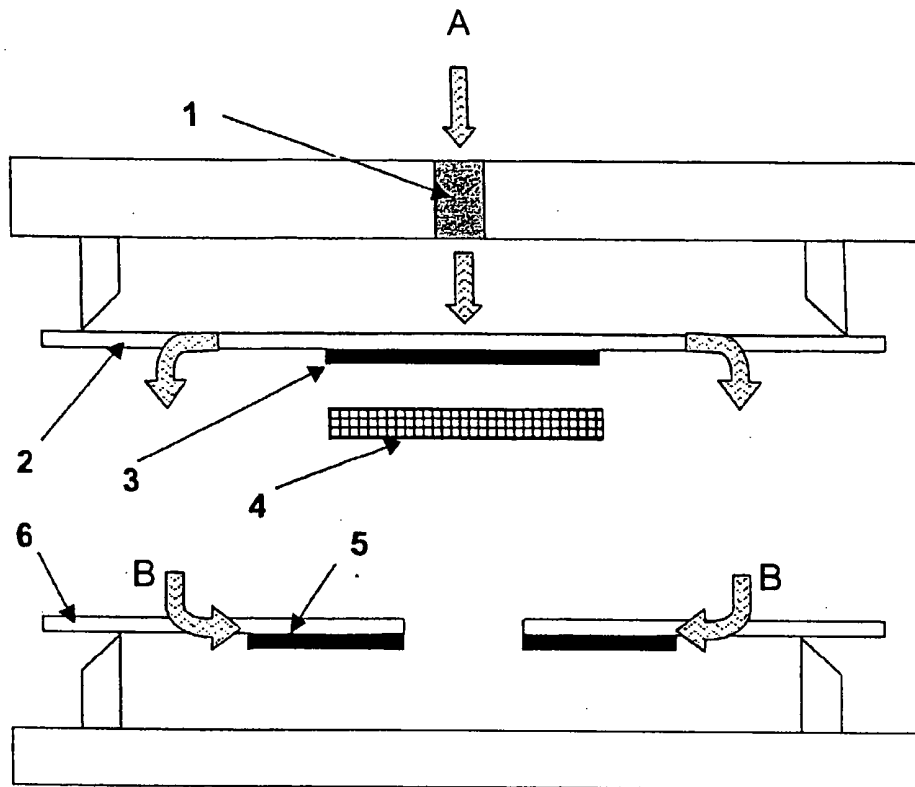
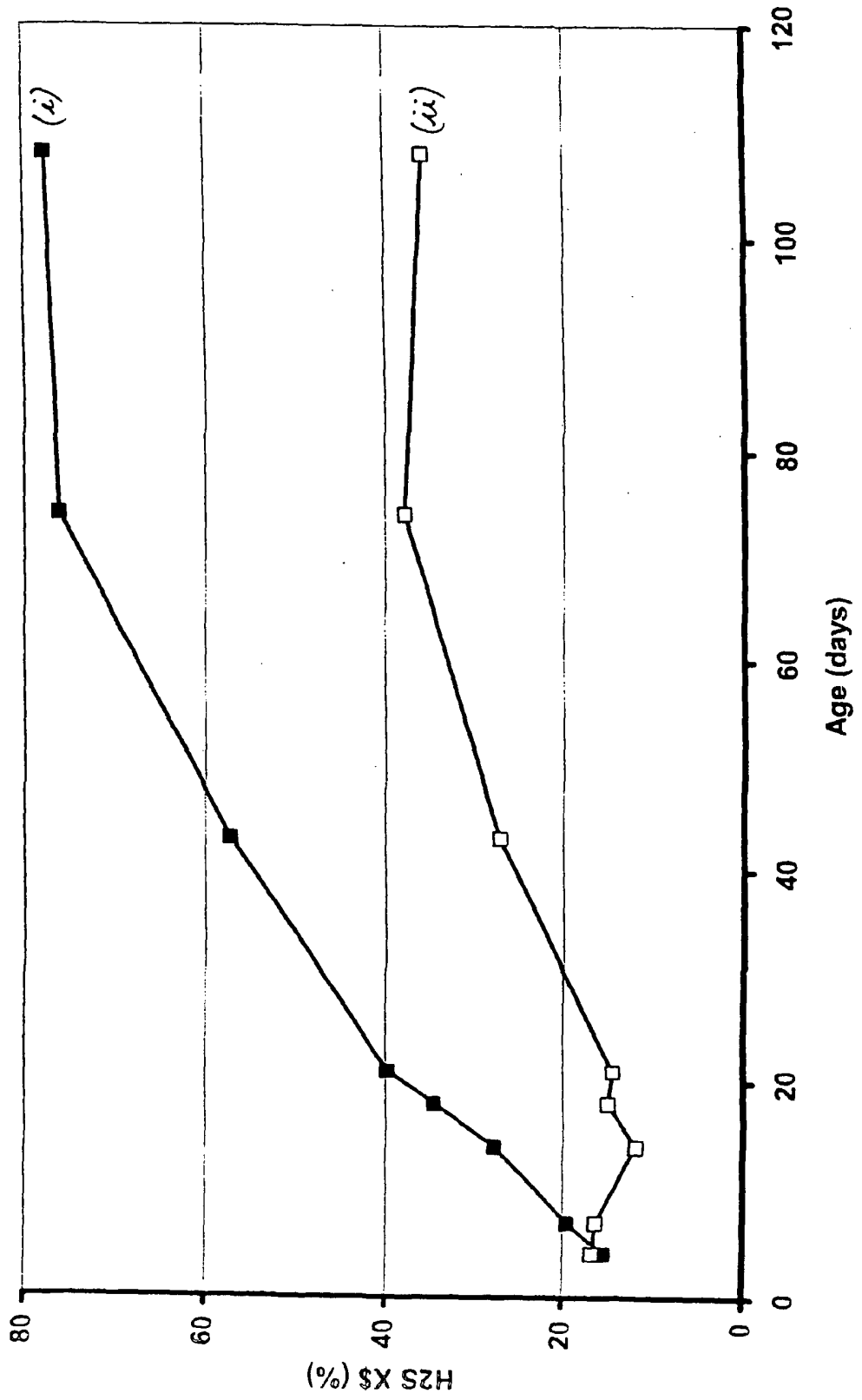


Fig. 1

Fig. 2



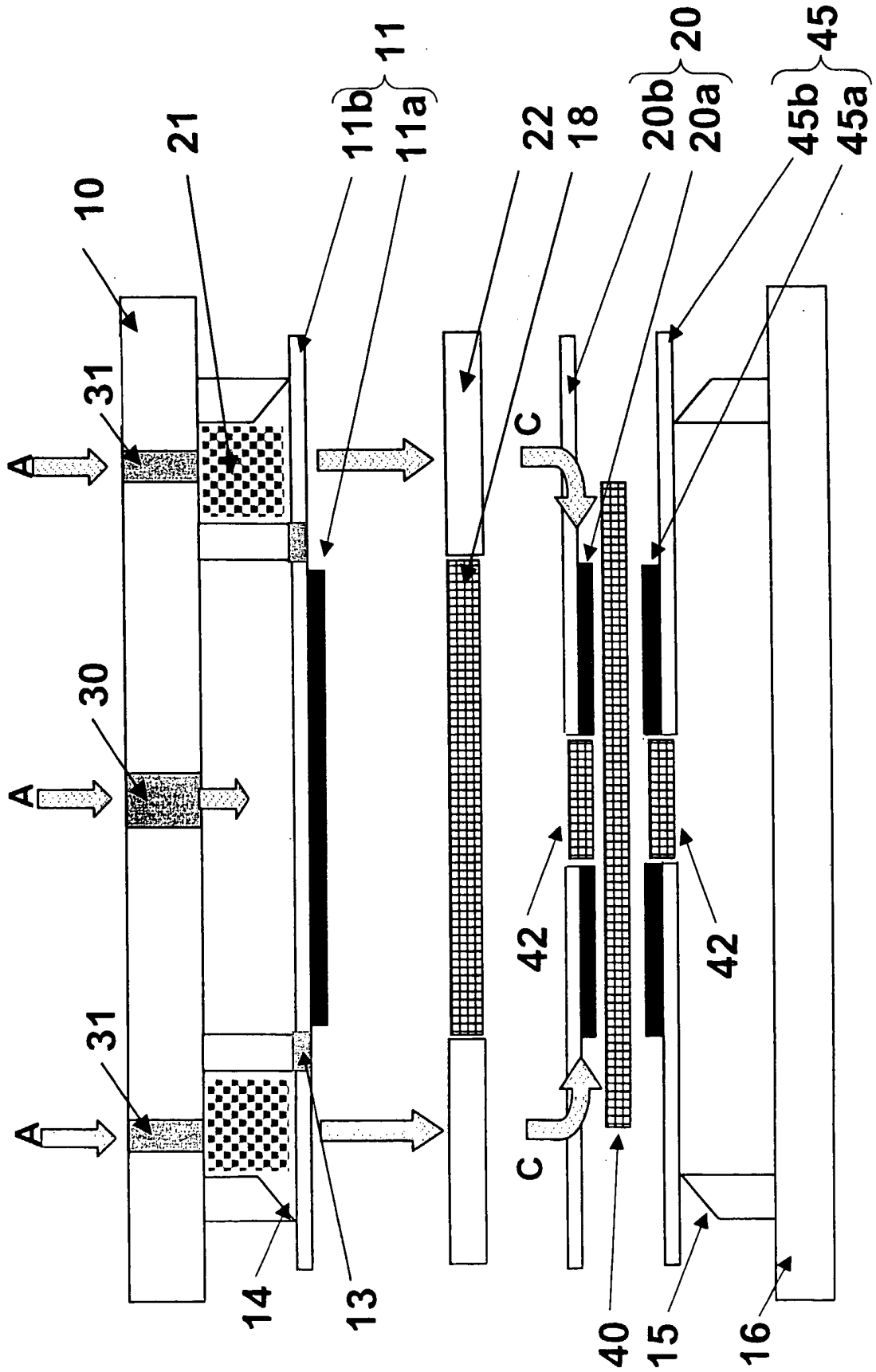
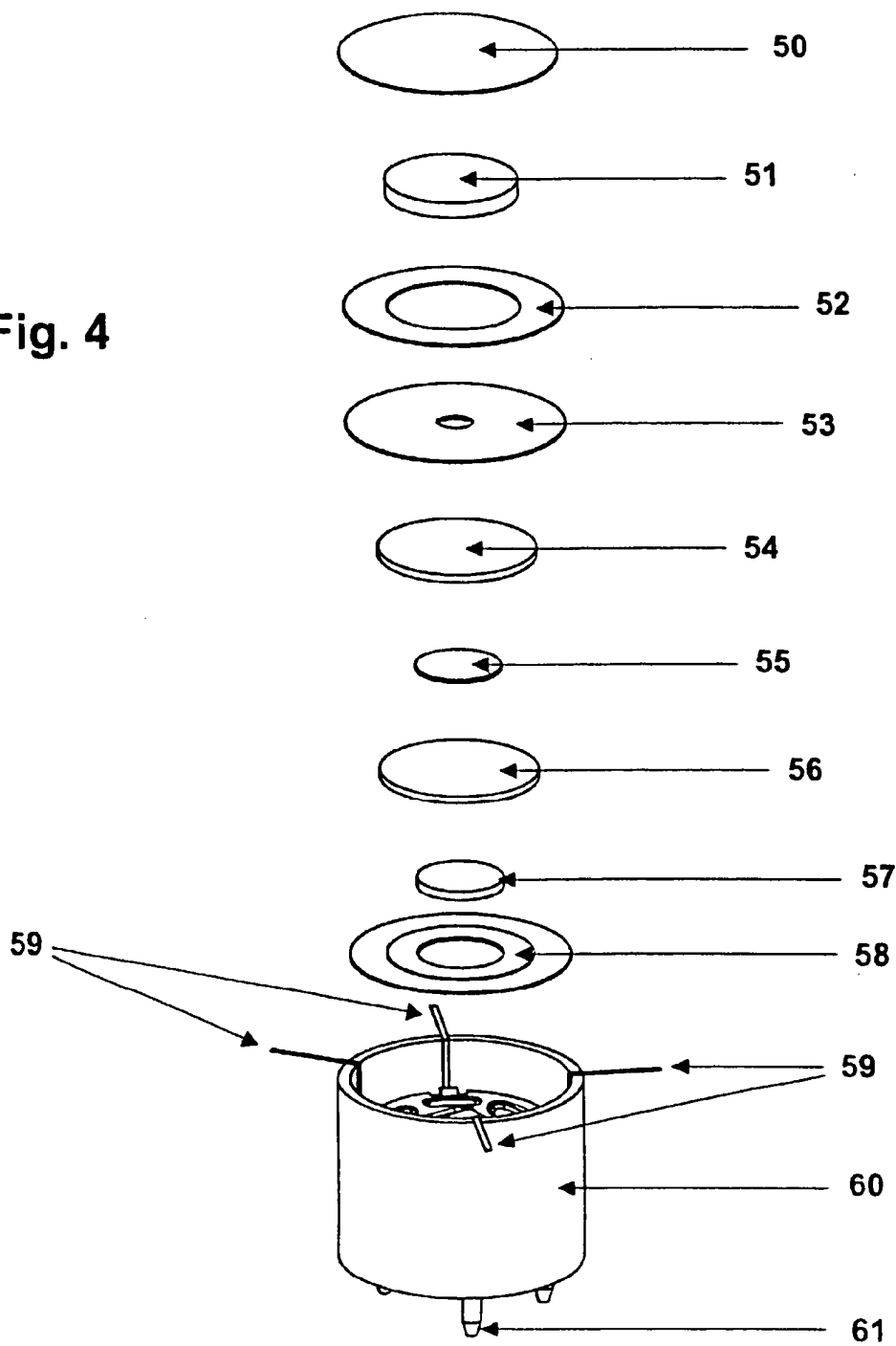


Fig. 3

Fig. 4



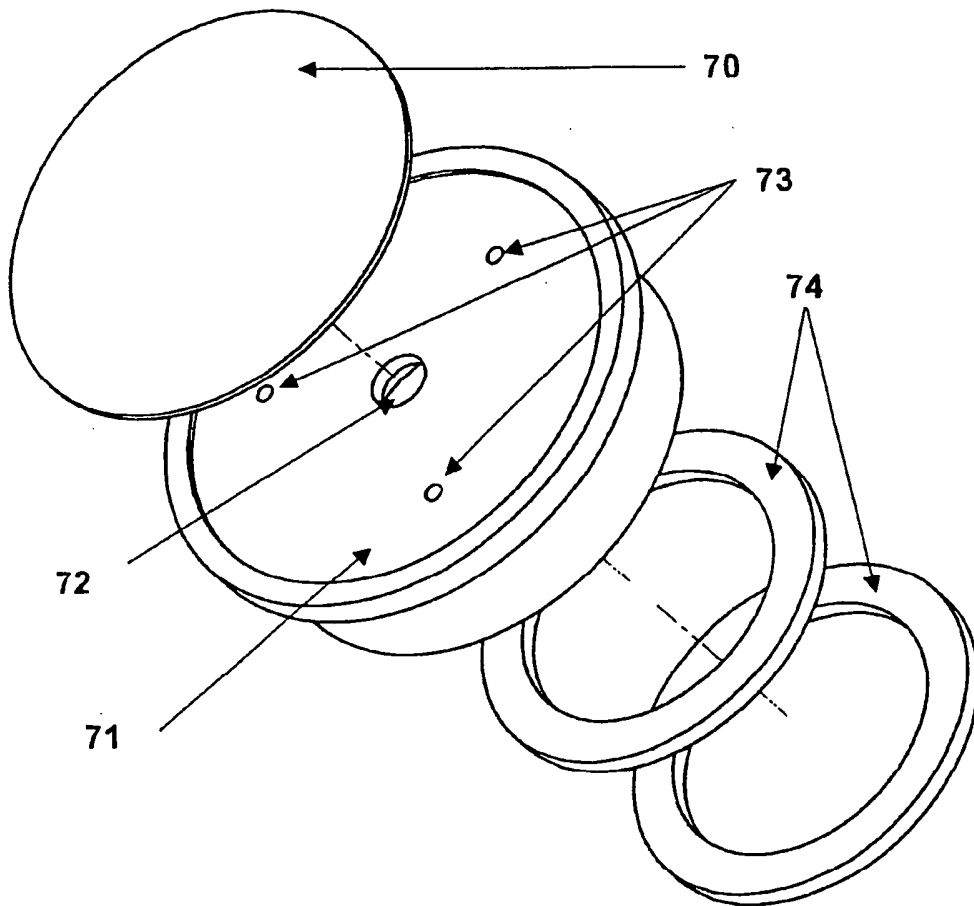


Fig. 5

Fig. 6

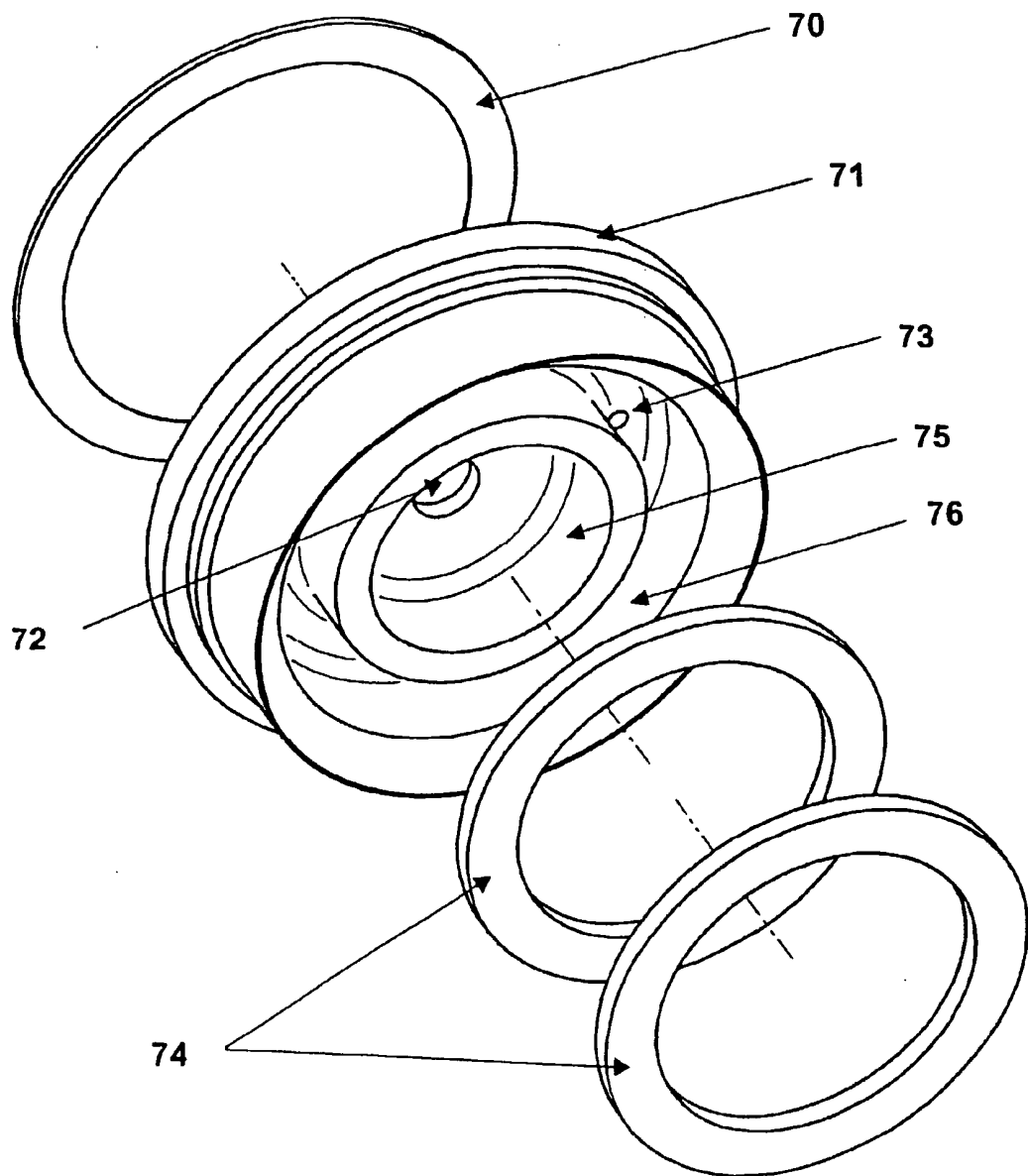
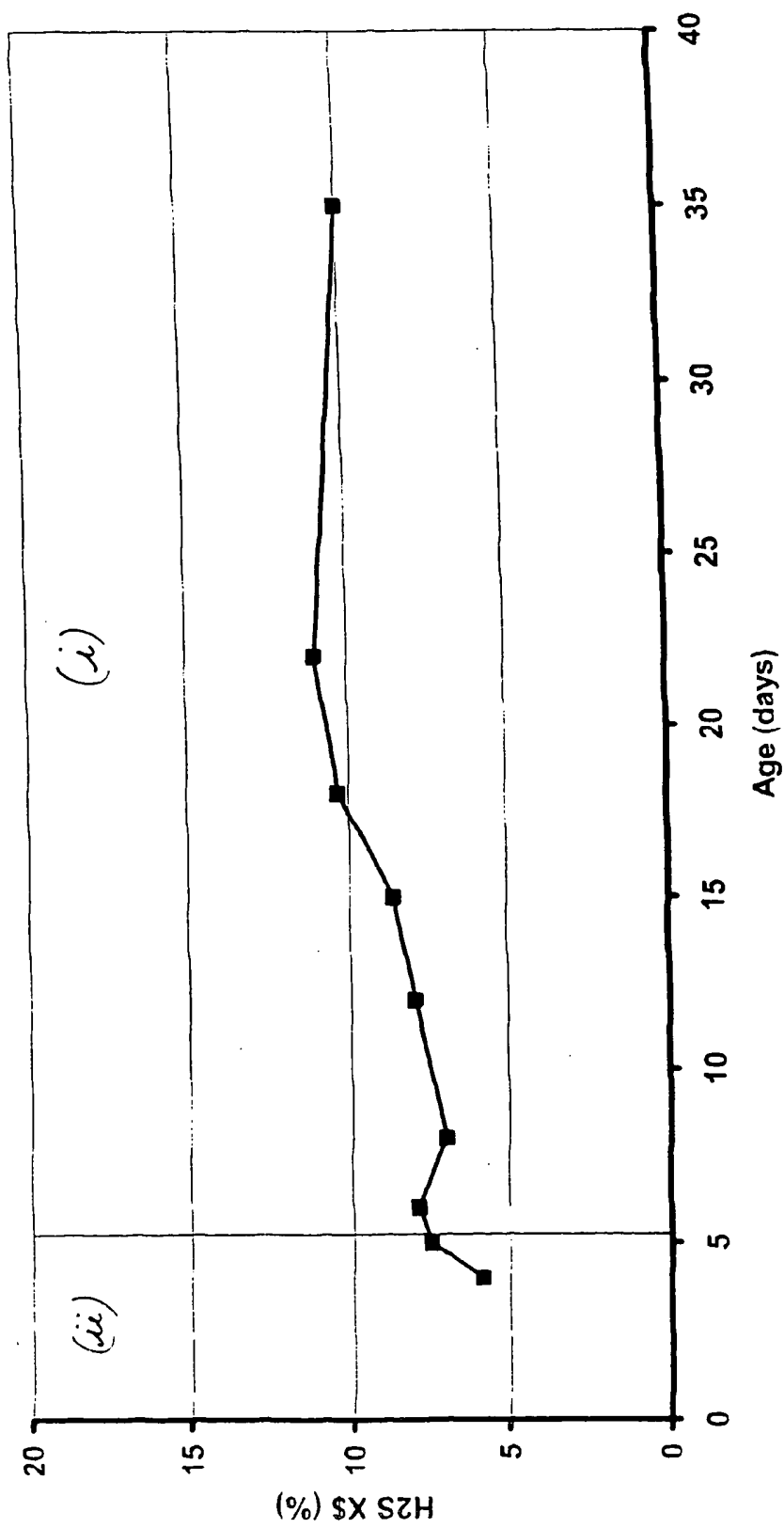


Fig. 7



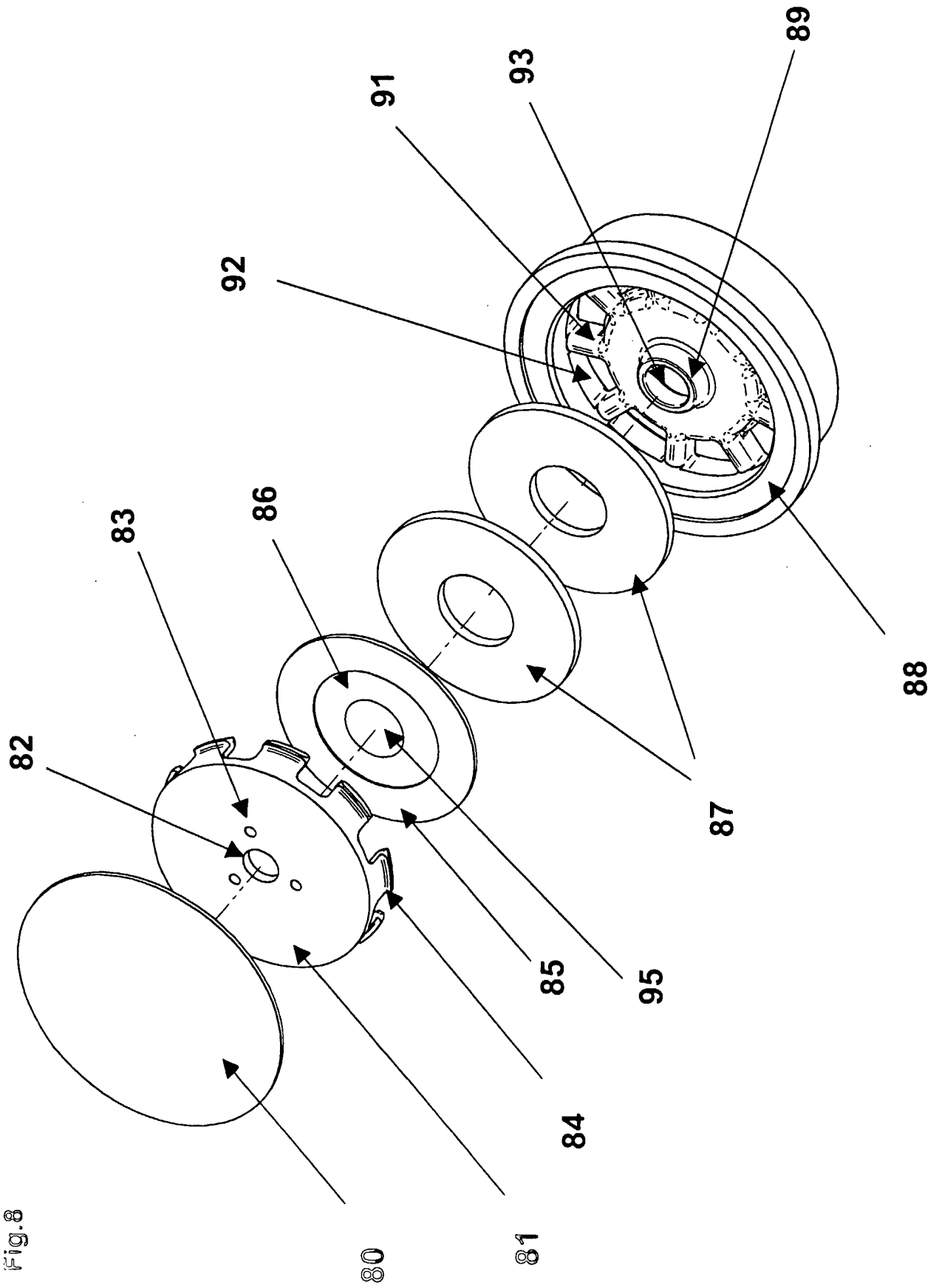


Fig. 8

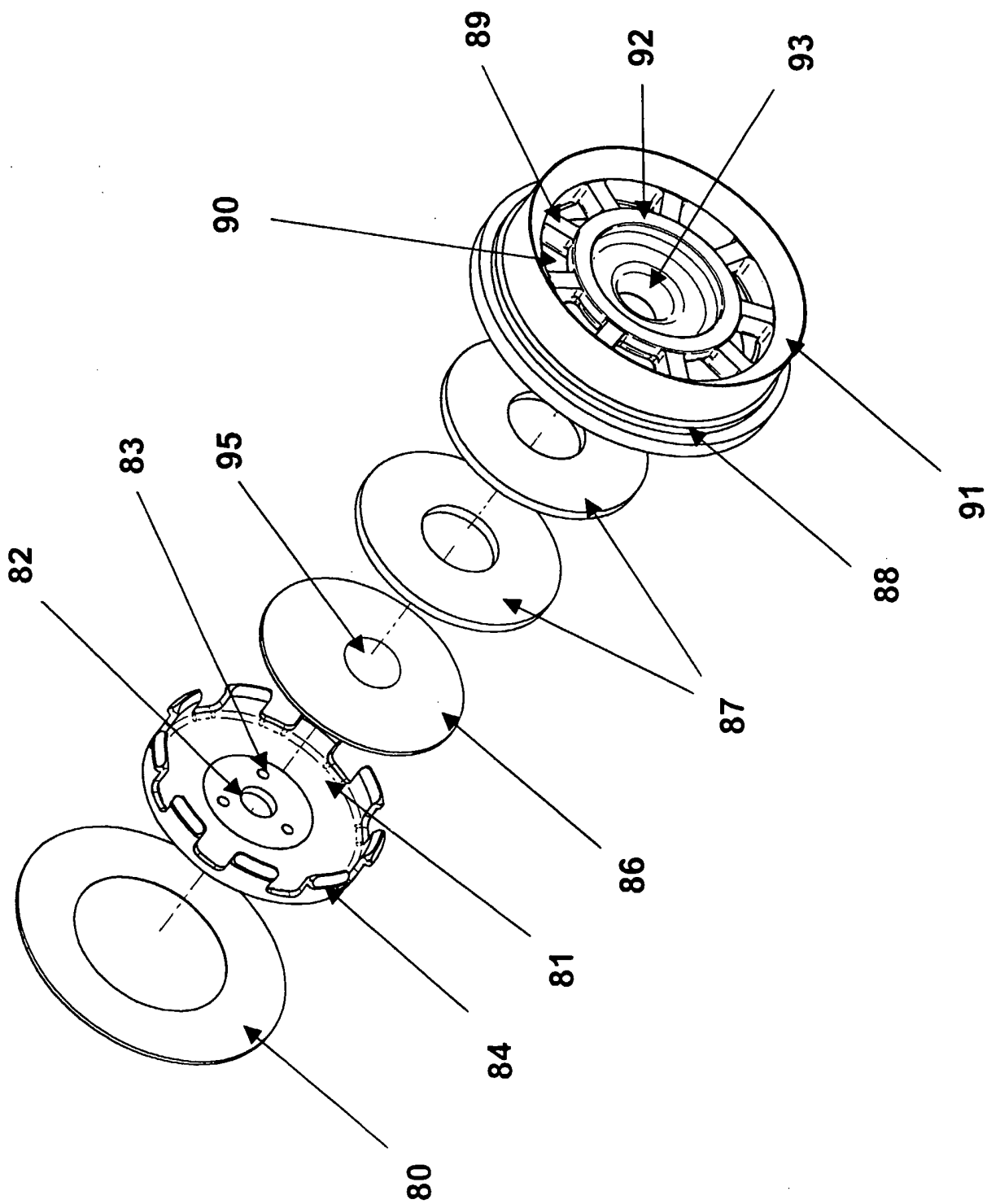


Fig.9

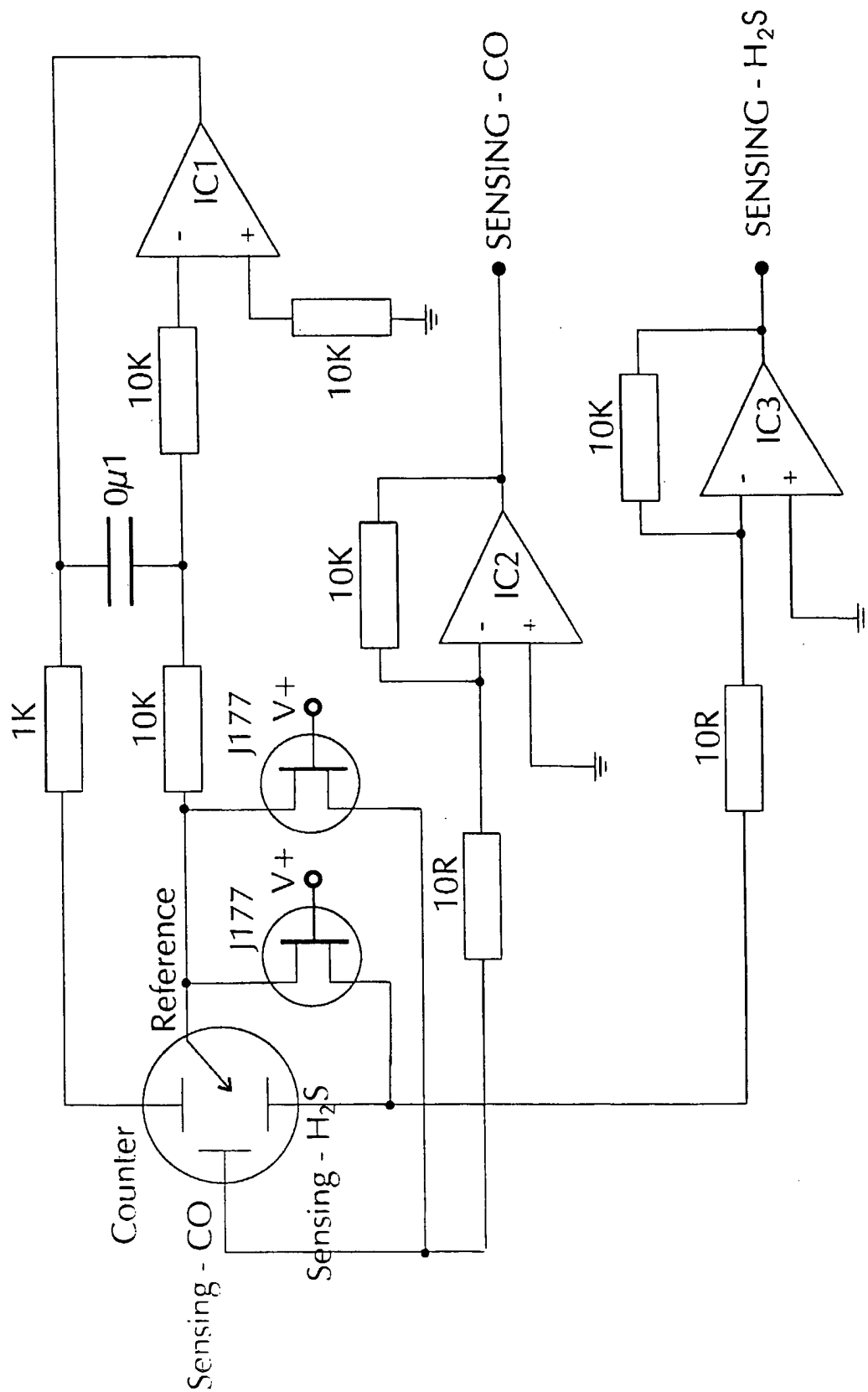


Fig. 10

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2004/002929

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 G01N27/49				
According to International Patent Classification (IPC) or to both national classification and IPC				
B. FIELDS SEARCHED				
Minimum documentation searched (classification system followed by classification symbols) IPC 7 G01N				
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched				
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal				
C. DOCUMENTS CONSIDERED TO BE RELEVANT				
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
Y	DE 40 41 143 C (W. SCHAPER) 12 March 1992 (1992-03-12) cited in the application the whole document -----	1, 2, 8, 16, 17, 20, 23, 25-27, 29		
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<table style="width: 100%; border: none;"> <tr> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. </td> <td style="width: 50%; border: none;"> <input checked="" type="checkbox"/> Patent family members are listed in annex. </td> </tr> </table>			<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.	<input checked="" type="checkbox"/> Patent family members are listed in annex.
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A document defining the general state of the art which is not considered to be of particular relevance *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *&* document member of the same patent family			
Date of the actual completion of the international search <p style="text-align: center; font-size: 1.2em;">30 September 2004</p>		Date of mailing of the international search report <p style="text-align: center; font-size: 1.2em;">12/10/2004</p>		
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <p style="text-align: center; font-size: 1.2em;">Duchatellier, M</p>		

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International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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