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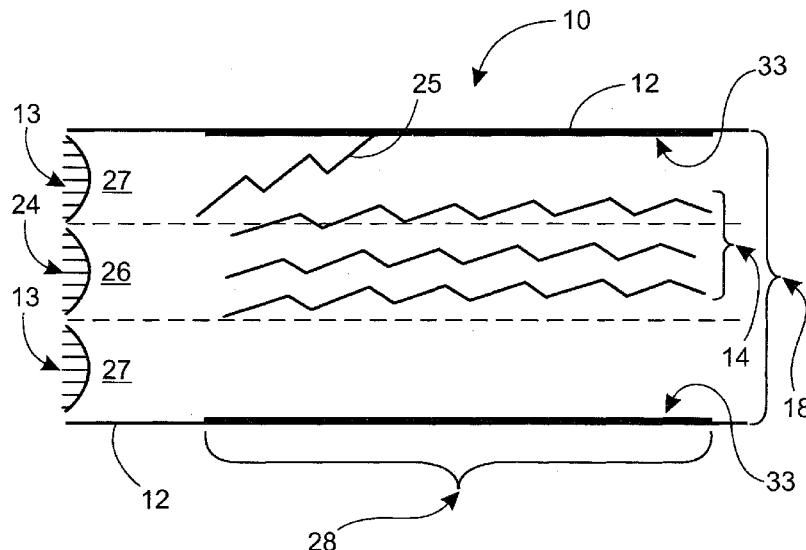


Fig. 3

(57) Abstract: The invention relates to a method for chemical analysis, in which a gas flow is ionized, the ionized gas flow (24) is led to a filtering area (28) fitted to the flow channel (18), the ionized gas flow is filtered using the DMS/FAIMS method, in order to remove at least some of the ions (25, 105) from the gas flow. A parallel mainly non-ionized gas flow (13), which is on at least one side of the ionized gas flow, is led to the filtering area together with the ionized gas flow. The invention also relates to a corresponding structure.

METHOD AND STRUCTURE FOR CHEMICAL ANALYSIS

The present invention relates to a method for chemical analysis, in which

5 - a gas flow is ionized,
 - the ionized gas flow is led to a planar filter structure fitted to the flow channel,
 - the ionized gas flow is filtered using the DMS/FAIMS method, in order to remove at least some of
10 the ions from the gas flow.

The invention also relates to a corresponding structure.

Figure 1 shows an idealized diagram of the principle of the known FAIMS (Field Asymmetric-waveform Ion-Mobility Spectrometry) aka DMS (Differential Mobility Spectrometry) ion-filtering technique. It is used, for example, to separate different types of ions in a gaseous form. The technique is based on using a high-frequency variable electric field in the ion-filter structure. The filter structure consists of, for 20 example, a substrate 102 arranged to form a flow channel 18 and planar filter electrodes 103 arranged on it facing each other.

The structure permits the passage of only ions 104 that behave in a specific manner in an electric field and filters other 25 ions 105 by neutralizing them electrically. The neutralization removes the ions, because the terminal velocity received by the ions in the electric field depends on the field's strength. In an asymmetrical field, the ions oscillate in the filter at an asymmetrical velocity, which causes a net transfer of ions 30 towards the electrodes in an advantageous direction relative to the field. The electrical-field-dependence of the ions is very small and this difference can be compensated by increasing the DC component CV to the frequency-changing field, which cancels a specific type of field dependence.

By arranging the ion-transporting gas flow between two parallel electrodes 103, and setting an electrical field of the type referred to above between these electrodes, some of the ions 105 can be removed through the structure thus obtained and the 5 desired passband can be selected with the aid of the aforementioned compensation voltage. By using an electric field after the filter in the flow direction to collect the ions 104 that have passed through the filter, it is possible to determine the quality and/or number (reference number 16 in 10 Figures 1 and 6 - 8) of the ions 104 that have passed through.

For its part, Figure 2 shows a situation corresponding more to reality in the case of the behaviour of the ions in the aforementioned filtering technique. The flow profile 101 of the 15 gas flow shows that the ionized gas flow to be analysed covers the entire cross-section area of the flow channel 18. As the ions are distributed evenly over the flow channel 18, the filter electrodes 103 will inevitably also collect ions 104b that it is particularly desired to pass through the filter. 20 These ions 104b, which are too close to the edge of the flow channel 18, are neutralized and thus out of the flow that has passed through the filter. This reduces the signal obtained from the system comprising the filter, and also the signal-noise ratio.

25

The present invention is intended to create a method and structure, which will improve the signal obtained from chemical analysis. The characteristic features of the method according to the invention are stated in Claim 1 and those of the 30 structure in Claim 9.

In the invention, a parallel mainly non-ionic gas flow, which is on at least one side of the ionized gas flow, is led along with the ionized gas flow to the filter structure. The use of 35 the solution prevents, or at least reduces, the filtering of ions that it is wished to pass through the filtering. In

addition to the measurement signal obtained, the signal-noise ratio of the measurement signal in chemical analysis is also improved.

5 According to one embodiment, the ionized gas flow can be led to the planar filter structure between a mainly non-ionized gas flow. In this case, the non-ionized gas flow is formed on both sides of the ionized gas flow, so that the flows create a kind of sandwich structure. Ion filtering implemented using the
10 DMS/FAIMS principle can thus be operated in the so-called second-order manner.

According to one embodiment, the ionized gas flow can also be flattened by the mainly non-ionized gas flow before both are
15 led to the planar filter structure. In this way, the performance of the filtering can be further improved.

By means of the invention, it is possible to solve, for example, a problem relating to planar DMS/FAIMS filtering, in
20 which some of the ions in the air or gas flowing in the flow channel of the filter structure are so close to the edge of the flow channel that they end up on the DMS/FAIMS collection electrodes, even though they should not. By using the shield flow according to the invention, for example on both sides of
25 the ion flow in which one is interested, as a kind of sandwich structure, only the ions to be filtered end up on the collection electrodes and are neutralized, whereas the desired ions passing through the filter remain advantageously in the middle of the flow channel. Thus, stated generally, the
30 invention is the use of a shield flow as a factor preserving the signal, i.e. improving the signal-noise ratio. The actual measurement signal can be measured only outside the DMS filter and after it, in one way or another. The other characteristic features of the invention and other advantages achieved with
35 the invention, are examined in more extensively in the description portion.

In the following, the invention, which is not restricted to the embodiments disclosed hereinafter, is described in greater detail with reference to the accompanying figures, in which

5

Figure 1 shows a schematic diagram of the principle of DMS/FAIMS

filtering, in an ideal situation,

Figure 2 shows a schematic diagram of drawbacks in 10 the operation of a filter according to the prior art, and the behaviour of ions in it,

Figure 3 shows a rough schematic diagram of the 15 operating principle of the filtering structure according to the invention, and the behaviour of ions in it,

Figure 4 shows schematically one embodiment of the 20 construction of the filter according to the invention,

Figure 5 shows schematically a second embodiment of 25 the construction of the filter,

Figures 6 and 7 show a few ways of bringing the flows to the filter structure,

Figure 8 shows examples of the dimensions of one 30 filter structure, and

Figures 9a and 9b show yet a third way to bring the flows to 35 the filter structure.

In the following, the method according to the invention for chemical analysis is described with reference to Figures 3 - 7.

30 The term chemical analysis can refer to, for example, the qualitative and/or quantitative detection from a gas flow of substances or similar structural units in the gas flow. An aerosol, in which particles are suspended in a gas, can also be considered to be a gas flow within the context of the 35 invention.

Figure 3 shows schematically on a very rough level an example of the solution according to the invention and the behaviour of the ions in a filter structure 10. The so-called second-order solution according to the invention is based on the idea of 5 taking a planar ionized gas flow 24 to a planar filtering area 28 at one edge of or in the middle of a flow channel 18. In other words, the ionized gas flow 24, which is the object of the filtering, is narrower in relation to the height of the whole flow channel 18.

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A description of the method can start, for example, from the ionization of the gas flow to be analysed. Ionization can take place, for example, outside the flow channel 18, in which case the ions are brought from the actual source to the flow channel 15 18 along with the gas flow. Ionization of the gas flow can be performed, for example, in some manner of the prior art that is, as such known, or is still under development. Some non-limiting examples are a radioactive ionizer, a corona charger, the electrospray technique, or some other well-known method. 20 The distance from the ionizer (not shown) to the entry opening of the flow-channel structure 18 is set to be relatively short, to reduce losses.

Next, the ionized gas flow 24 is led to the flow channel 18 25 forming the filter structure 10. A parallel, mainly non-ionized gas flow 13 is formed on at least one side of the ionized gas flow 24 already when it is led into the flow channel 18, or only inside the actual flow channel 18. In any event, the parallel, mainly non-ionized gas flow 13 is formed before the 30 ionized gas flow 24 is taken to filtering in the filtering area 28. Thus, in the invention, the gas flow 24 to be analysed is formed from a part flow that is narrower relative to the height of the flow channel 18. In this way, a kind of 'shield flow' 13 is created on at least one side of the ionized gas flow 24, in 35 the flow direction between the gas flow 24 and the wall 12 of the flow channel 18. The use of the shield flow 13 makes it

possible, for example, to reduce the neutralization of the edge ions 25 of the ion flow 24 that is intended for later analysis.

Figure 3 shows the flow zones 26, 27 of the gas flows 13, 24 5 and their flow profiles. Now the neutral, i.e. mainly non-ionized flows 13 are on both sides relative to the ionized flow 24. Thus the flows 13, 24 form a sandwich structure. Each flow 13, 24 can be separated from the other by a structure (not shown), which divides the flow channel 18 planarly into parts, 10 before the filtering area 28.

Next, the ionized gas flow 24 is led to the filtering area 28 arranged in the flow channel 18, in which the desired ions are filter out of it. The parallel, mainly non-ionized gas flow 13, 15 which is on at least one side of the ionized gas flow 24, is led to the filtering area 28 along with the ionized gas flow 24. In this case, the ionized gas flow 24 is led to the filtering area 28 in between the mainly non-ionized gas flow 13, which is thus on both sides of the ionized gas flow 24.

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Next, the ionized gas flow 24 is filtered using the DMS/FAIMS method to remove at least some of the ions 105 from the gas flow 24. As such, in terms of the electric fields used in it, the implementation of the DMS/FAIMS filtering will be obvious 25 to one skilled in the art, and for this reason will not be dealt with further in this connection. In the filtering, the ions 25 intended to be filtered out of the ionized gas flow 24 arranged in the middle move in the filtering area 28 through the passage zones 27 formed by the shield flows 13 at the edges 30 of the flow channel 18 and are neutralized, because their field dependence causes them to move towards the filter electrodes 33. For its part, the ions 14 of the gas flow 24 passing the filtering have not time to move to the filter electrodes 33. In the middle of the flow channel 18 there is an oscillation zone 35 26 for the passing ions 14, which do not end up on the filtering area's 28 electrodes 33 in the filtering area 28.

Figures 4 - 7 show, in a roughly simplified form, some schematic structural solutions for implementing a filter structure 10 for chemical analysis, as cross-sections of the 5 flow channel 18 in its longitudinal, i.e. flow direction. The structure 10 includes a flow-channel arrangement 18 for the ionized gas flow 24. The gas flow 24 is arranged to be filtered in the structure 10 using the DMS/FAIMS method in a planar filtering area 28 fitted to the flow channel 18. The filtering 10 area 28 includes two DMS/FAIMS electrodes 33, which can be controlled in a manner that is, as such, known, using known control means (not shown). The structure 10 includes means 11 for creating a mainly non-ionized gas flow 13 on at least one side of the ionized gas flow 24.

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In the embodiment shown in Figure 4, the means 11 include a structure 11 dividing the gas flow 18 into parts before the filtering area 28. By means of the structure 11, several narrower flow channels, whose height is only part of the height 20 of the entire flow channel 18, are formed in the flow channel 18. By means of the structure 11, the ionized gas flow 24 intended to be analysed can be arranged in the middle of the flow channel 18, with the mainly non-ionized, i.e. neutral gas flows 13 on both sides relative to it. By means of the channel 25 structure 11, the neutral, i.e. shield-flows 13 are kept separate from the ionized flow 24 in the middle.

In the embodiments of Figures 4 - 7, the structure 10 includes two longitudinal walls 11 in the direction of the flow channel 30 18 fitted to the flow channel 18. The walls 11 too are planar.

The mainly non-ionized gas flow 13 and the ionized gas flow 24 are combined with each other before they are led to the filtering area 28. For this purpose a small gap 19 is arranged 35 to remain that is free of the dividing structures 11, between the structure 11 dividing the flow channel 18 into parts and

the filtering area 28. Of course, the non-ionized gas flow 13 and the ionized gas flow 24 can be combined with each other already when they are brought to the flow channel 18, but they may then mix with each other detrimentally before the filtering area 28 to such an extent as to impair the result of the filtering.

Figures 5 - 7 show a second embodiment of the filter structure 10. In it the mainly non-ionized gas flow 13 is used to flatten 10 the ionized gas flow 24 on both sides, when they are led to the filtering area 28. One way to implement this is to arrange a throttle structure 15 in the filtering area 28 in order to flatten the ionized gas flow 24 using the mainly non-ionized gas flow 13. The structure 15 is now implemented by means of a 15 material layer fitted over the entire length of the filtering area 28, which reduces the height of the flow channel 18 in the filtering area 28. The structure 15 is in a substrate 12 on opposite edges of the flow channel 18. For their part, the DMS/FAIMS electrodes 33 are now on the surfaces of the material 20 layer 15 opposite each other.

The structure-free gap 19 remaining between the divider structure 11 and the filtering area 28 now permits the side flows 13 to turn and the combined flow 24* will fit to go to 25 the filtering area 28. The flattening of the effective flow 24 in the middle, achieved by the turning of the side flows 13, improves performance. The entry-side edge 15a of the throttle structure 15 is vertical. Optimally, however, these shapes can be slightly curved or bevelled, so that the sharp corners will 30 not cause problems.

Figures 6 and 7 show schematic examples of how the flows 13, 24 can be brought to the filter structure 10 and thus also to the flow channel 18. In addition, the figure shows schematically 35 the analyser 16 that comes after the filter structure 10. The gas flows 13, 24 can be brought to the structure 10 from

different sides of it, or even from the same side, depending on the implementation.

In the embodiment of Figure 6, the mainly non-ionized gas flow 13 is formed by bringing a neutral shield-gas flow 13 to the flow channel 18. If the filter structure 10 is examined in its typical operating attitude, in which the electrodes 33 are on the upper and lower surface of the flow channel 18, the ionised flow 24 is brought to the filter structure 10 from its end, without no change in direction. The neutral flows 13 are brought to the filter structure 10 from above it and below it.

The embodiment of Figure 7 shows an example of the embodiment, in which a narrow ion flow 24 is created by neutralizing the side flows 13. Now the gas flows to be brought to the filter structure 10 can all be the same ionized gas flow 24' brought from the ionizer and, for example, led from above to the filter structure 10 in its typical operating attitude. In this case, the mainly non-ionized gas flow 13 is formed by neutralizing part of the gas flow 24' only once it is in the flow channel 18. To neutralize the side flows 13, the structure 11 dividing the flow channel 18 into parts is fitted with electrode means 38 by means of which are arranged to neutralize part of the ionized gas flow 24' brought to the flow channel 18, to create mainly non-ionized gas flows 13. This embodiment has the advantage of simple implementation. When creating an ionized flow 24 and a neutral flow 13 with the aid of the structure 10, there is no need at all for 'clean' flows as shields and for bringing to the structure 10.

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In both embodiments, the flows 24, 13 after the divider structure 11 arranged in the flow channel 18 are combined to form a single flow 24', so that the ionization flow 24 remains as its own narrow band relative to the cross-section of the channel 18, for example in the centre of the channel 18. A flow arrangement like that of the second order can be implemented

inside the DMS/FAIMS filter 10, when neutralization of the passage mobility will be reduced and the signal-noise ratio will improve. In a structure according to the invention like that of the second order, the flows can be arranged as shown in 5 the figures and in such a way as to preserve the ionization zone 26, unless it is separately disturbed.

Figures 6 and 7 show schematically the flight 24a of ions in an analyser 16 in an electric field set for measurement. This does 10 not affect the flow profile, as the concentration is non-existent relative to the mass flow. A measurement field is created, or measurement is performed, using electrodes 16a and these have a counter electrode 16b. Using the electrodes, for example a mobility analysis of the ions is made, i.e. different 15 mobilities are directed to different electrodes by using either a permanent electric field, or by varying the magnitude of the electric field in such a way as to change the so-called boundary mobility coming to the electrode.

20 Figure 8 shows a further few examples of the dimensions, or dimension ratios of the structure 10. The length L_{DMS} of the DMS electrodes 33, i.e. of the area 28, in the flow direction, i.e. the longitudinal direction of the structure 10, can be, for example 10 - 80 mm. The height D of the flow channel 18 can be, 25 for example, 1 - 10 mm. The thickness W of the throttle structures 15 of the whole height H of the flow channel 18 can be, for example, 25 - 75%. The height S of the sub-flow channels formed by the divider structures 11 can be, for example, 0.1 - 2 mm. The ratio between the height D of the flow 30 channel 18 and the sub-channels can be $D > 3S$, but, however, preferably $D < 10S$.

The thickness W of the throttle structures 15 in the area of the DMS/FAIMS electrodes 33 can be 50 - 90% of the height S of 35 the side-flow channels. The throttle plates 15 narrow the

filter area 28 on the entry side, which flattens the combined flow 24* after the divider structures 11.

Figures 9a and 9b show yet another way of bringing the flows 5 13, 24 to the filter structure 10. Figure 9b shows a cross-section of the filter structure 10 of Figure 9a, seen from the end, from the entry point of the gas flows 13, 24 to the structure 10. In this embodiment, the flows 13, 24 are brought to the filter structure 10 from the side, if the filter 10 structure 10 is examined in its typical operating attitude, when the electrodes 33 are in the upper and lower walls 12 of the flow channel 18. The particular advantage of this embodiment is in the manufacture of the filter structure 10, especially when the parts of the piece 10 are made using 15 injection moulding, or some other method that permits the entire set of channels to be made from a single part. When the gas flows 13, 24 are brought to the filter structure 10 in this way, the gas-flow connections can be easily arranged in the filter structure 10.

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In the embodiment, the ionized gas flow 24 is brought from one side of the filter structure 10 to the sub-channel delimited by the wall structures 11 fitted to the flow channel 18. The non-ionized shield flows 13 are, for their part, brought to the 25 filter structure 10 from the opposite side, to the under channels delimited by the wall structures 11 fitted to the flow channel 18 and the outer wall 12 of the flow channel 18. One other way would be to bring all the flows 13, 24 from the same side of the structure 10.

30

The side flows 13 are arranged in such a way that a middle flow 24 forms the narrow and flattened part in the middle of the channel 18. According to one embodiment, the flows 13, 24 can be of the same magnitude (the same mass flow) in the same-sized 35 sub-channels. However, one measure of the quality of the device 10 can be the narrowness (the narrower the better) of the flow

24 in the middle, relative to the total flow. The height of the side channels can be altered with the mass flows, in such a way that the flow velocities in the different channels are more or less the same. In that case, turbulence and spreading of the 5 middle flow 24 will not take place when the flows 13, 24 combine. The use of single-size channels can be an optimum, in which the same mass flow produces the same velocities in all the single-size channels. Channels of different sizes are not, however, excluded, as in the practice device the large side- 10 flow channels can, in some cases, be a significant advantage. The ratio of the flow quantities of the middle channel and the side channels can be 1:2, or even 1:200. In other words, 200 litres per minute would flow from the side channels, while 1 litre per minute would flow from the middle, but in that case, 15 the dimensions should, of course, be quite large.

It must be understood that the above description and the related figures are only intended to illustrate the present invention. The invention is thus in no way restricted to only 20 the embodiments disclosed or stated in the Claims, but many different variations and adaptations of the invention, which are possible within the scope on the inventive idea defined in the accompanying Claims, will be obvious to one skilled in the art.

CLAIMS

1. Method for chemical analysis, in which
 - a gas flow is ionized,
 - the ionized gas flow (24) is led to a filtering area (28) fitted to the flow channel (18),
 - the ionized gas flow (24) is filtered using the DMS/FAIMS method, in order to remove at least some of the ions (25, 105) from the gas flow (24),
- 10 characterized in that a parallel mainly non-ionized gas flow (13), which is on at least one side of the ionized gas flow (24), is led to the filtering area (28) together with the ionized gas flow (24).
- 15 2. Method according to Claim 1, characterized in that the ionized gas flow (24) is led to the filtering area (28) between the mainly non-ionized gas flow (13).
- 20 3. Method according to Claim 1 or 2, characterized in that the mainly non-ionized gas flow (13) is formed in the flow channel (18).
- 25 4. Method according to Claim 3, characterized in that
 - an ionized gas flow (24') is brought to the flow channel (18),
 - the mainly non-ionized gas flow (13) is formed in the flow channel (18) by neutralizing part of the ionized gas flow (24').
- 30 5. Method according to any of Claims 1 - 4, characterized in that the mainly non-ionized gas flow (13) is formed by bringing a neutral gas flow to the flow channel (18).
- 35 6. Method according to any of Claims 1 - 5, characterized in that the mainly non-ionized gas flow (13) and the ionized gas

flow (24) are combined with each other before being led to the filtering area (28).

7. Method according to any of Claims 1 - 6, characterized in 5 that the ionized gas flow (24) is flattened by the mainly non-ionized gas flow (13) when they are led to the filtering area (28).

8. Method according to any of Claims 1 - 7, characterized in 10 that at least part of the gas flow (13, 24) is brought from the sides into the filtering structure (10), when it is in the operating attitude.

9. Structure for chemical analysis, which includes a flow-15 channel arrangement (18) for an ionized gas flow (24), which is arranged to be filtered using the DMS/FAIMS method in a planar filtering area (28) fitted to the flow channel (18), characterized in that the structure (10) includes means (11) for creating a mainly non-ionized gas flow (13) on at least one 20 side of the ionized gas flow (24).

10. Structure according to Claim 9, characterized in that the means include a structure (11) dividing the flow channel (18) into parts, in the middle of which can be arranged the ionized 25 gas flow (24) and the mainly non-ionized gas flows (13) on both sides of relative to it.

11. Structure according to Claim 10, characterized in that 30 electrode means (38), which are arranged to neutralize part of the ionized gas flow (24') brought to the flow channel (18), are fitted to the structure (11) dividing the flow channel (18) into parts, in order to create a mainly non-ionized gas flow (13).

35 12. Structure according to any of Claims 9 - 11, characterized in that a gap (19) is arranged to remain between the structure

(11) dividing the flow channel (18) into parts and the filtering area (28).

13. Structure according to any of Claims 9 - 12, characterized 5 in that the filtering area (28) includes a structure (15) for flattening the ionized gas flow (24) by the mainly non-ionized gas flow (13).

14. Structure according to any of Claims 9 - 13, characterized 10 in that at least part of the gas flows (13, 24, 24') is arranged to be brought from the sides into the filter structure (10) when it is in the operating attitude.

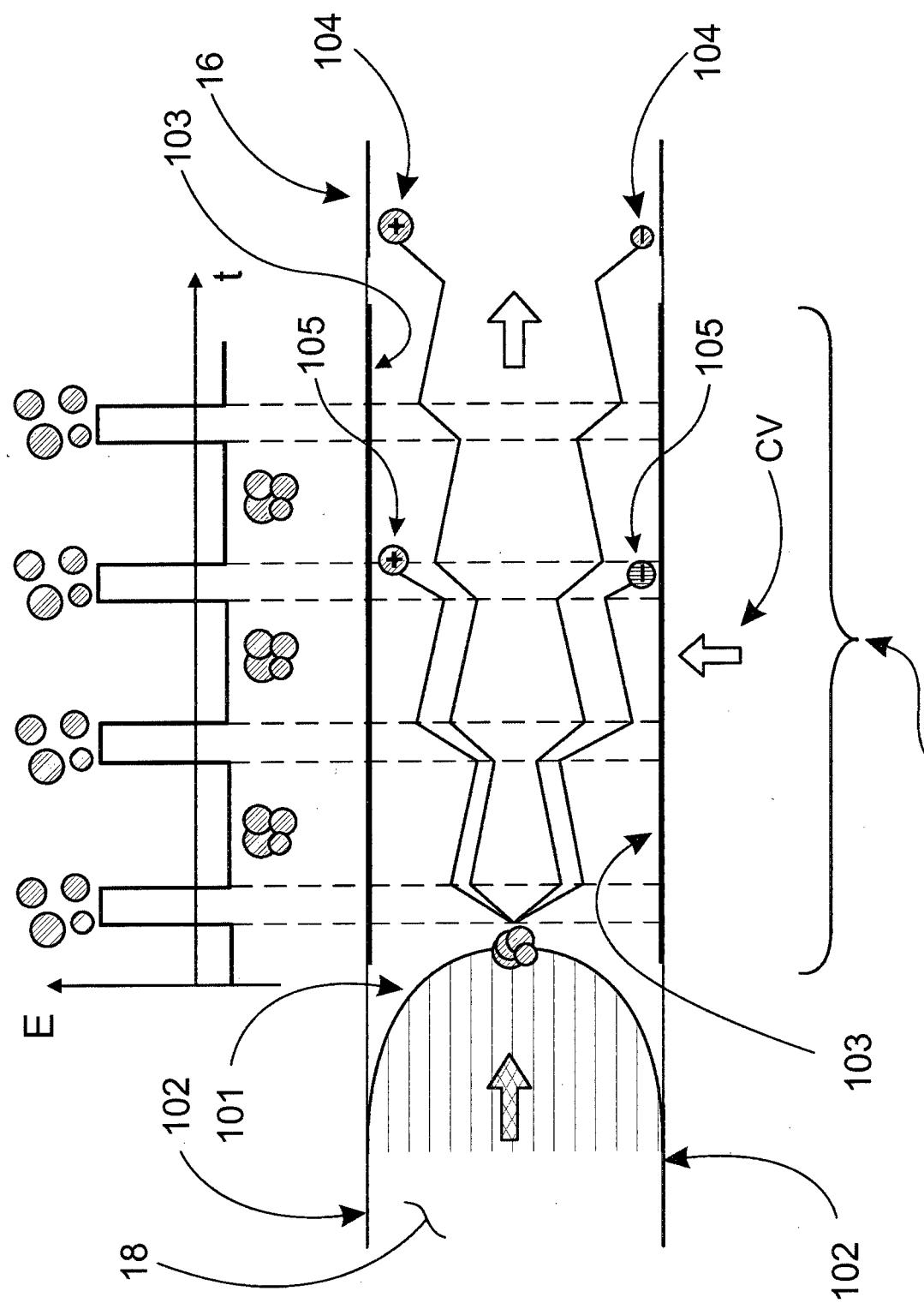


Fig. 1
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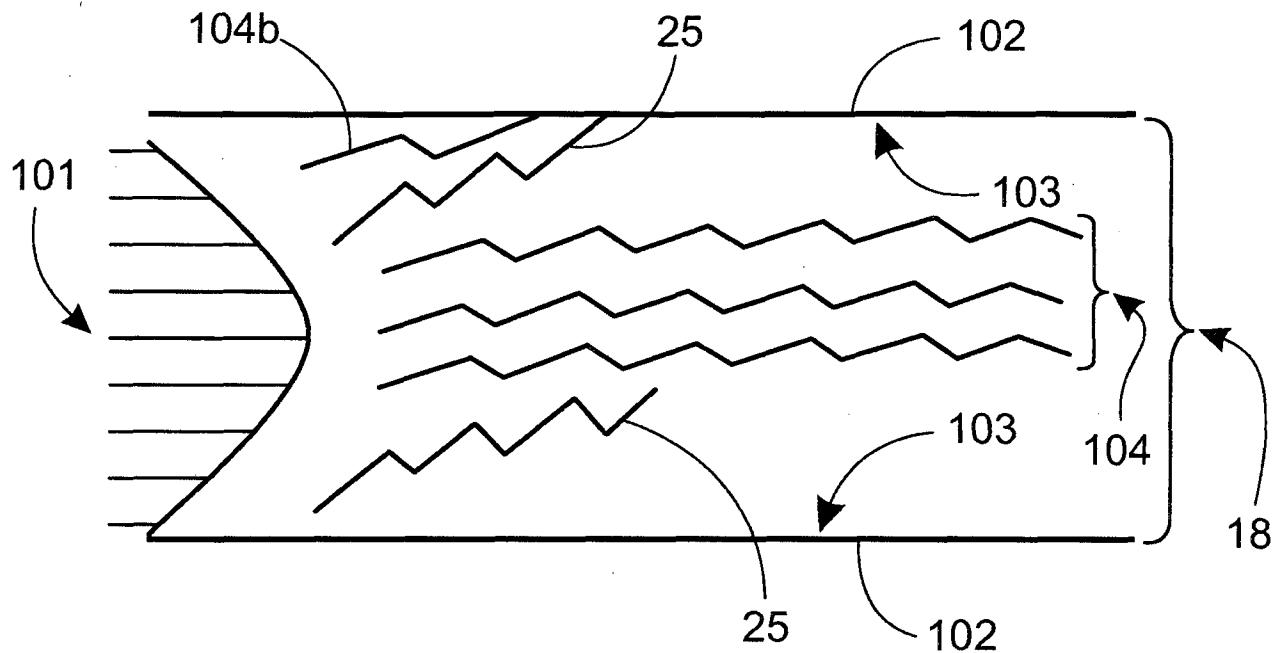


Fig. 2

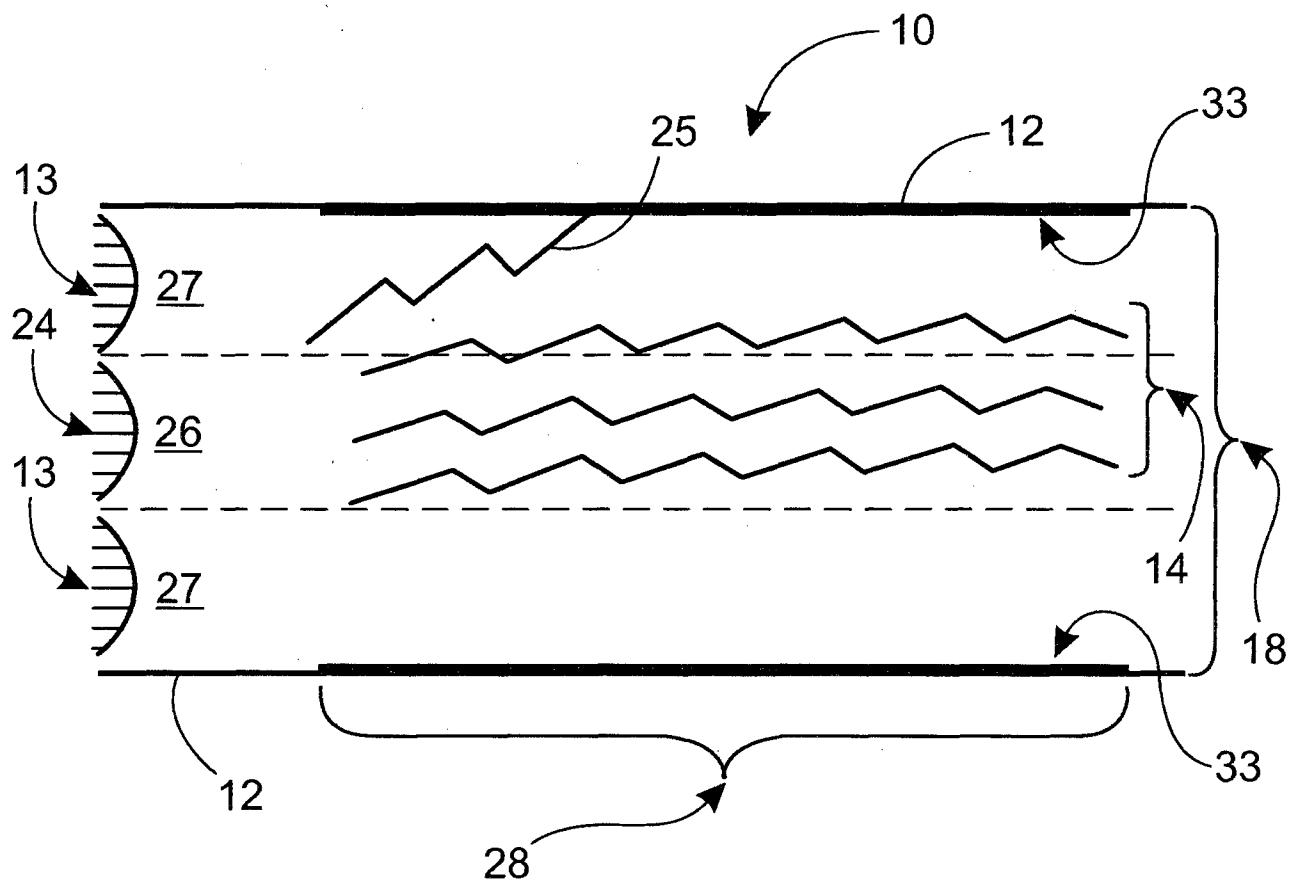


Fig. 3

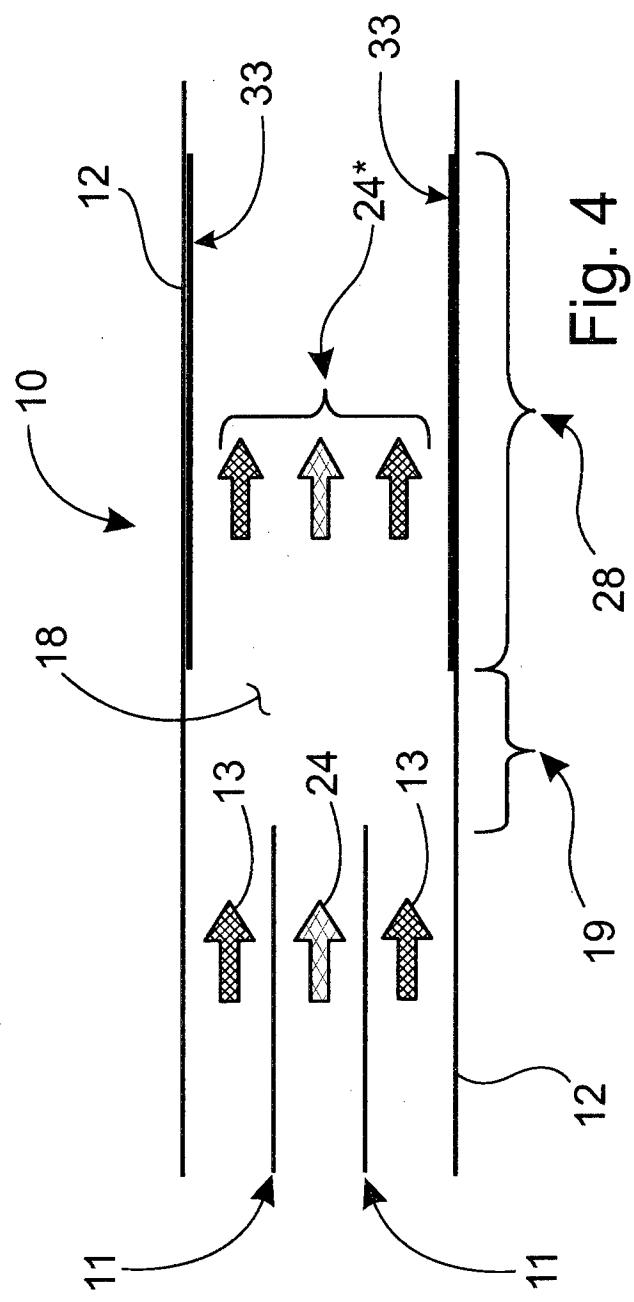


Fig. 4
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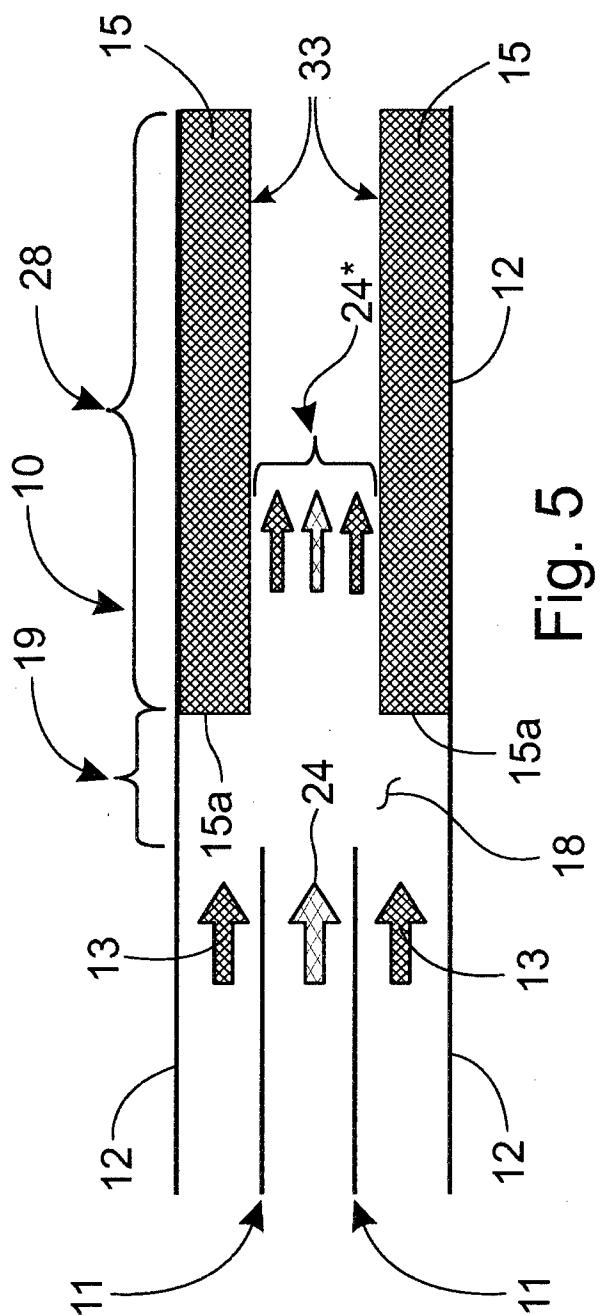


Fig. 5
15a 18 3

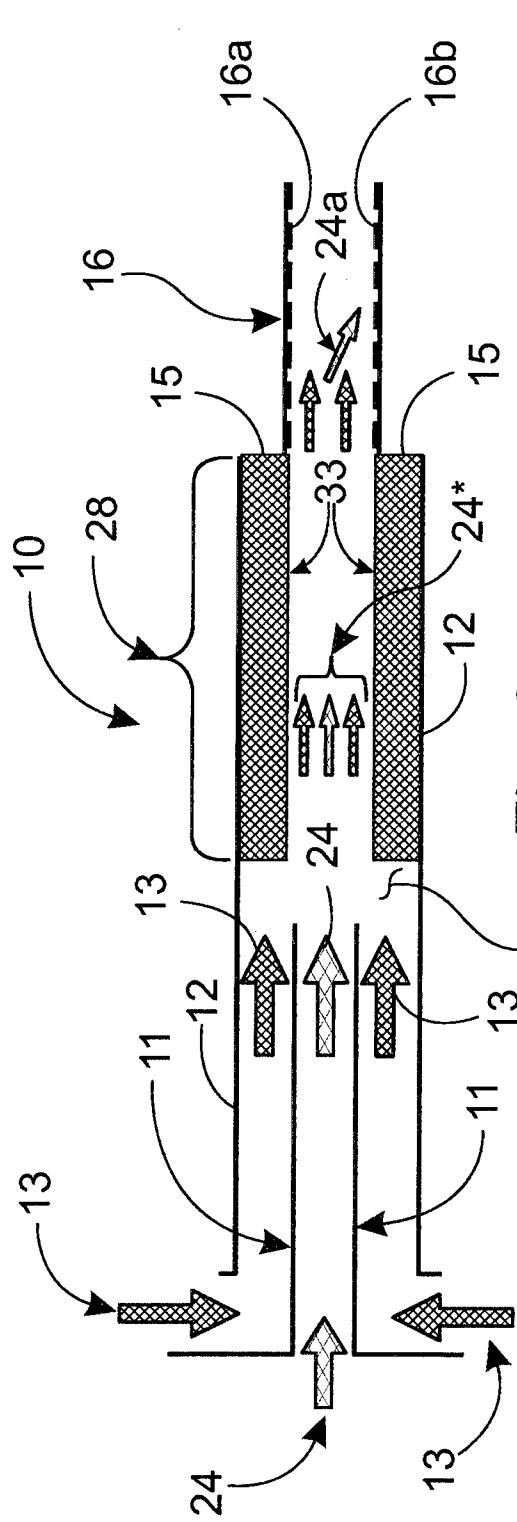


Fig. 6

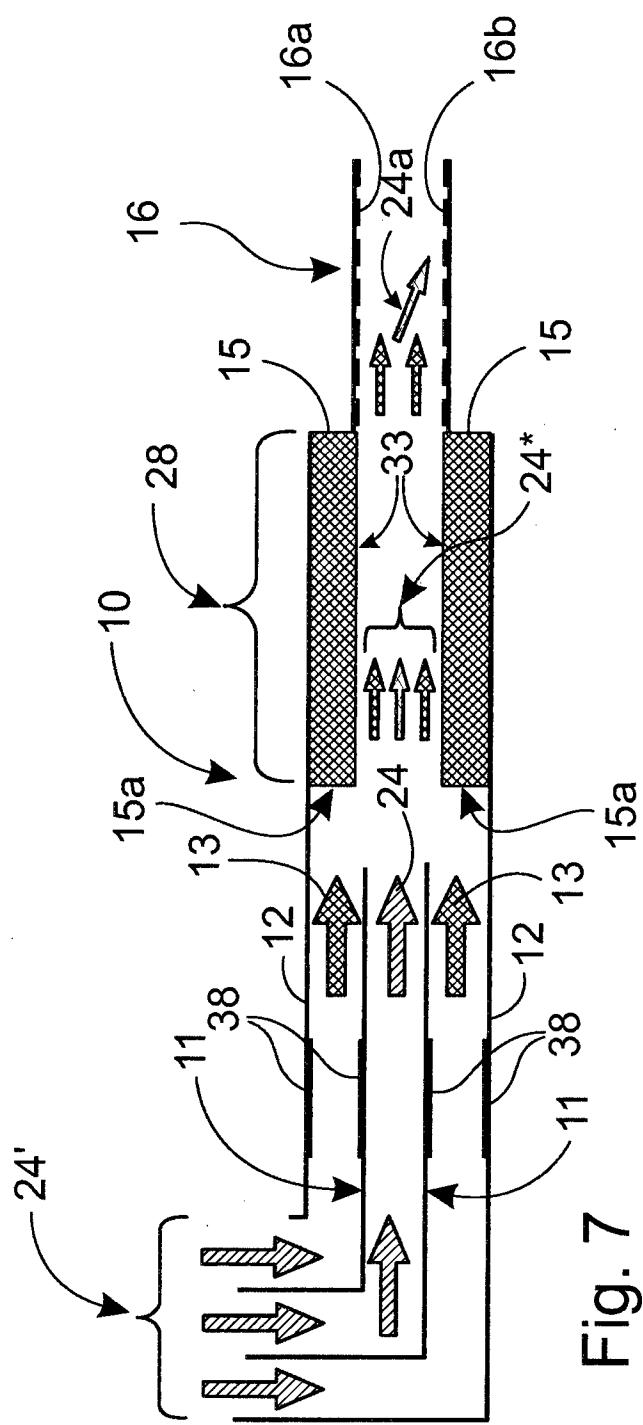


Fig. 7

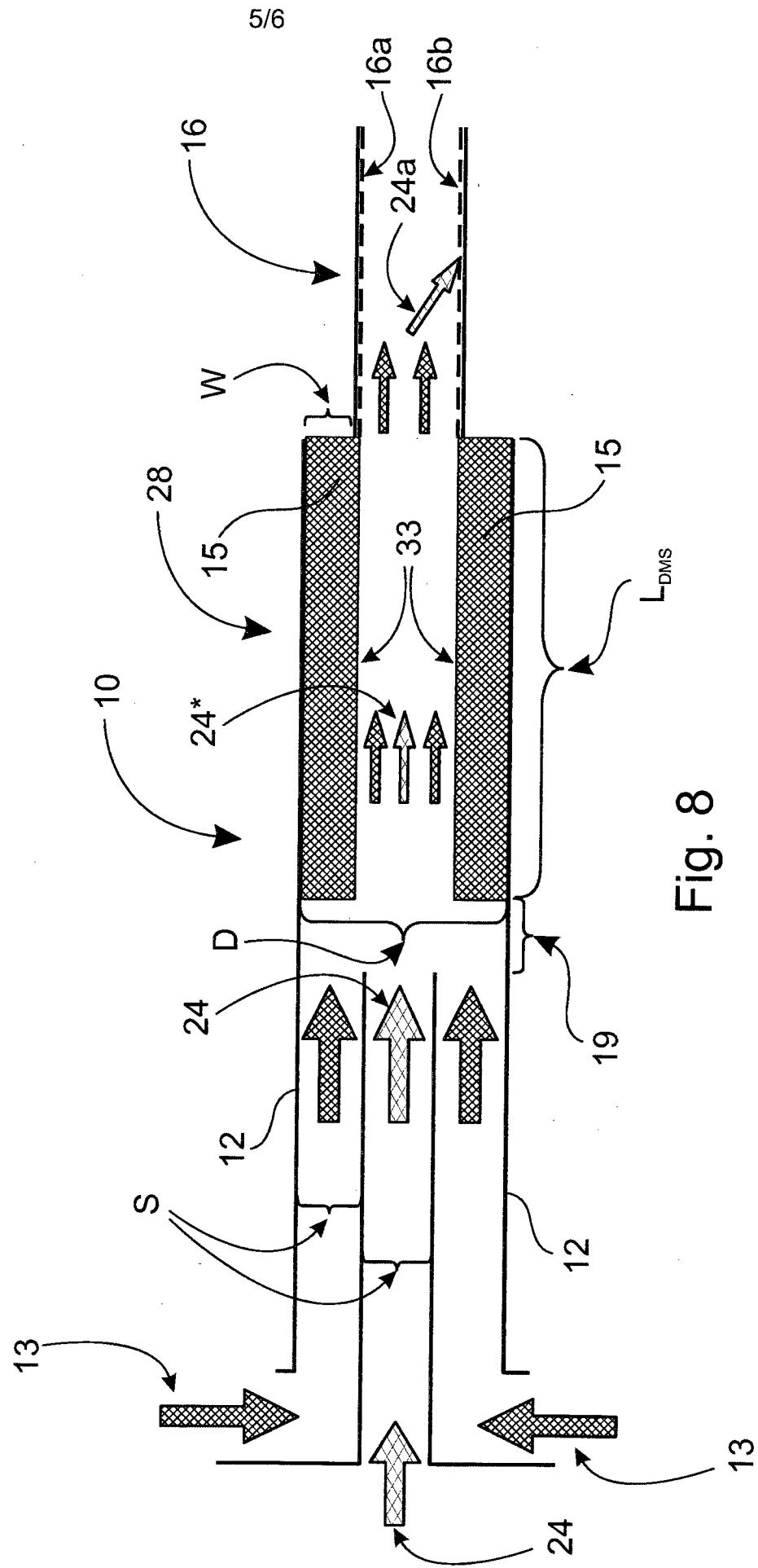


Fig. 8

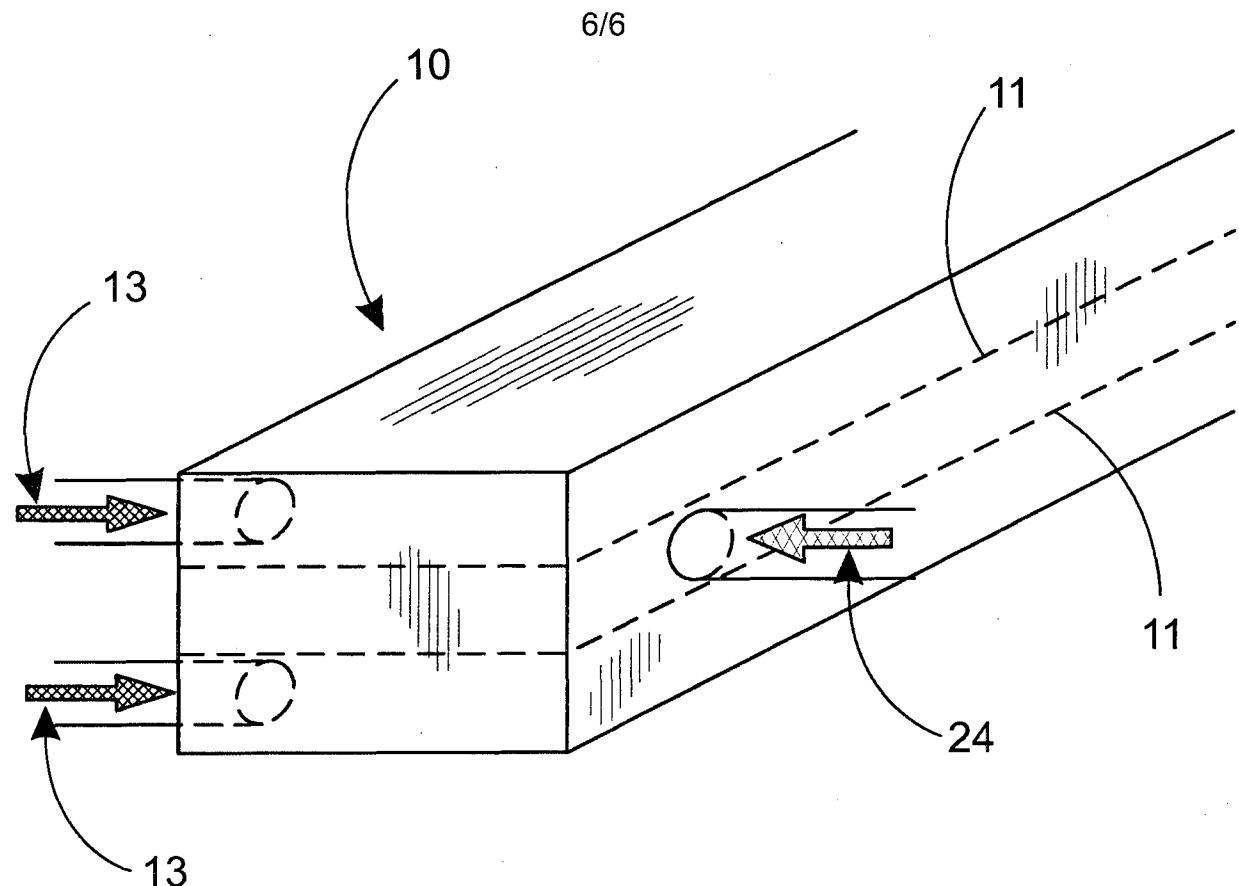


Fig. 9a

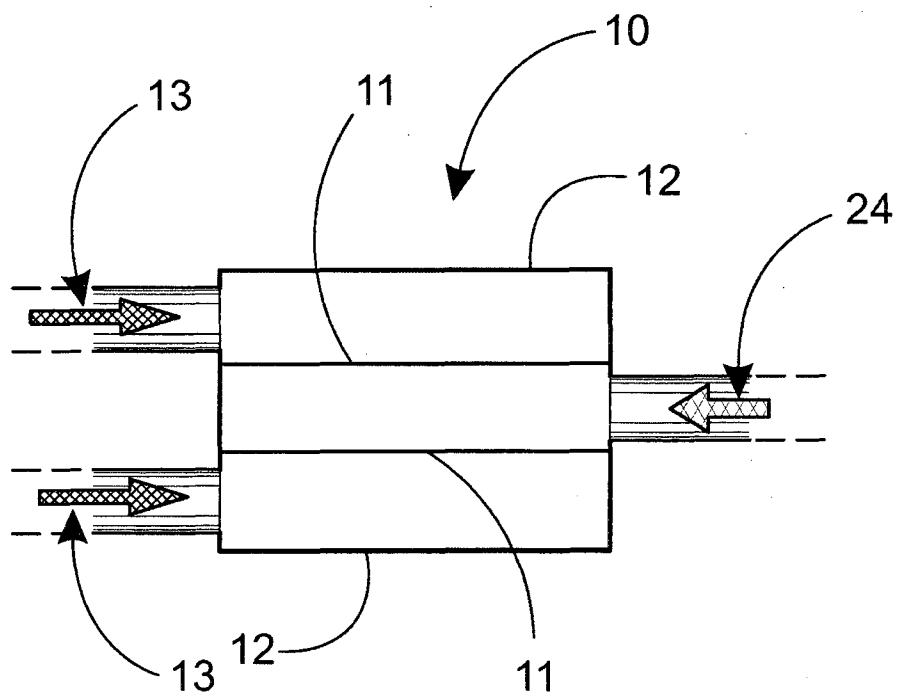


Fig. 9b

INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI2013/050440

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

FI, SE, NO, DK

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006097156 A1 (GUEVREMONT ROGER [CA]) 11 May 2006 (11.05.2006) paragraphs [0041], [0052], [0053], [0061], [0062]; Figs 1, 5, 6	1, 2, 5, 7-9, 14
X	US 2003150987 A1 (GUEVREMONT ROGER [CA] et al.) 14 August 2003 (14.08.2003) abstract; paragraph [0062]; Figs. 1 and 2f	1, 2, 5, 7-9, 14
X	US 2007023647 A1 (ZIMMERMANN STEFAN [DE] et al.) 01 February 2007 (01.02.2007) paragraphs [0015], [0020], [0058]; claim 1; Fig. 1	1, 2, 5, 7-10, 12-14
X	US 2006054804 A1 (WEXLER ANTHONY S [US]) 16 March 2006 (16.03.2006) the whole document, especially, paragraphs [0008], [0044]; Figs. 1 and 2	1, 6, 9

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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International application No.

PCT/FI2013/050440

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02071053 A3 (DRAPER LAB CHARLES S [US]) 03 January 2003 (03.01.2003) the whole document, especially, page 26, line 7 - page 27, line 11; Fig. 6	1, 6, 9

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No. PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
US 2006097156 A1	11/05/2006	AT 345494 T AU 2003249796 A1 AU 2003264200 A1 AU 2003266054 A1 AU 2003266055 A1 AU 2003266900 A1 AU 2003266901 A1 CA 2499115 A1 CA 2499247 A1 CA 2499471 A1 CA 2499471 C CA 2499474 A1 CA 2499474 C CA 2499476 A1 CA 2499476 C CA 2499538 A1 CA 2499538 C CA 2499570 A1 CA 2502445 A1 CA 2502445 C CA 2589335 A1 CA 2589335 C DE 60309725 D1 DE 60309725 T2 EP 1543320 A2 EP 1543320 B1 EP 1580793 A2 EP 1820204 A1 US 2005194527 A1 US 7041969 B2 US 2005269500 A1 US 7078678 B2 US 2006038119 A1 US 7084394 B2 US 2005194532 A1 US 7223971 B2 US 2006052960 A1 US 7225096 B2 US 2006151693 A1 US 7227132 B2 US 2006237643 A1 US 7274014 B2 US 2006038121 A1 US 7285774 B2 US 7358504 B2 US 2006049363 A1 US 7378651 B2 US 2006151694 A1 US 7417225 B2	15/12/2006 19/04/2004 19/04/2004 19/04/2004 19/04/2004 19/04/2004 19/04/2004 03/09/2005 03/09/2005 08/04/2004 24/11/2009 08/04/2004 04/05/2010 08/04/2004 02/06/2009 08/04/2004 24/11/2009 08/04/2004 08/04/2004 23/08/2011 01/06/2006 13/07/2010 28/12/2006 10/01/2008 22/06/2005 15/11/2006 28/09/2005 22/08/2007 08/09/2005 09/05/2006 08/12/2005 18/07/2006 23/02/2006 01/08/2006 08/09/2005 29/05/2007 09/03/2006 29/05/2007 13/07/2006 05/06/2007 26/10/2006 25/09/2007 23/02/2006 23/10/2007 15/04/2008 09/03/2006 27/05/2008 13/07/2006 26/08/2008

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
 PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		US 2007018629 A1	25/01/2007
		WO 2004029603 A2	08/04/2004
		WO 2004029604 A2	08/04/2004
		WO 2004029614 A1	08/04/2004
		WO 2004030022 A2	08/04/2004
		WO 2004030023 A2	08/04/2004
		WO 2004030129 A2	08/04/2004
		WO 2006056049 A1	01/06/2006
<hr/>			
US 2003150987 A1	14/08/2003	AT 308043 T	15/11/2005
		AT 308751 T	15/11/2005
		AU 5143999 A	28/02/2000
		AU 5144099 A	28/02/2000
		AU 5144199 A	28/02/2000
		AU 5144399 A	28/02/2000
		AU 2003201232 A1	02/09/2003
		AU 2003203089 A1	02/09/2003
		AU 2003203090 A1	02/09/2003
		AU 2003203091 A1	02/09/2003
		AU 2003203092 A1	02/09/2003
		AU 2003244484 A1	02/09/2003
		AU 2003244485 A1	02/09/2003
		AU 2003244486 A1	02/09/2003
		CA 2260572 A1	05/02/2000
		CA 2273322 A1	05/02/2000
		CA 2273322 C	18/11/2008
		CA 2339548 A1	17/02/2000
		CA 2339548 C	10/07/2007
		CA 2339549 A1	17/02/2000
		CA 2339549 C	14/10/2008
		CA 2339552 A1	17/02/2000
		CA 2339553 A1	17/02/2000
		CA 2339553 C	18/11/2008
		CA 2474561 A1	14/08/2003
		CA 2474564 A1	14/08/2003
		CA 2474564 C	28/09/2010
		CA 2474566 A1	14/08/2003
		CA 2474584 A1	14/08/2003
		CA 2474586 A1	14/08/2003
		CA 2474586 C	19/04/2011
		CA 2474684 A1	14/08/2003
		CA 2474684 C	28/09/2010
		CA 2475555 A1	14/08/2003
		CA 2475608 A1	14/08/2003
		DE 69927983 D1	01/12/2005
		DE 69927983 T2	24/08/2006
		DE 69928111 D1	08/12/2005
		DE 69928111 T2	27/07/2006

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
 PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		EP 1102984 A1	30/05/2001
		EP 1102985 A1	30/05/2001
		EP 1102985 B1	26/10/2005
		EP 1102985 B8	26/04/2006
		EP 1102986 A1	30/05/2001
		EP 1102986 B1	02/11/2005
		EP 1102986 B8	11/01/2006
		EP 1391912 A2	25/02/2004
		EP 1474677 A2	10/11/2004
		EP 1474691 A1	10/11/2004
		EP 1474819 A1	10/11/2004
		EP 1481240 A1	01/12/2004
		EP 1481415 A1	01/12/2004
		JP 2010108941 A	13/05/2010
		JP 4990348 B2	01/08/2012
		JP 2002522873 A	23/07/2002
		US 2002134932 A1	26/09/2002
		US 6504149 B2	07/01/2003
		US 6621077 B1	16/09/2003
		US 6639212 B1	28/10/2003
		US 2003226965 A1	11/12/2003
		US 6713758 B2	30/03/2004
		US 2003230711 A1	18/12/2003
		US 6753522 B2	22/06/2004
		US 6770875 B1	03/08/2004
		US 2003150984 A1	14/08/2003
		US 6787765 B2	07/09/2004
		US 6831271 B1	14/12/2004
		US 6917036 B2	12/07/2005
		US 2005116160 A1	02/06/2005
		US 6987262 B2	17/01/2006
		US 2003150986 A1	14/08/2003
		US 6998608 B2	14/02/2006
		US 2005178962 A1	18/08/2005
		US 7005633 B2	28/02/2006
		US 2005161596 A1	28/07/2005
		US 7026612 B2	11/04/2006
		US 2004232326 A1	25/11/2004
		US 7034286 B2	25/04/2006
		US 2005151072 A1	14/07/2005
		US 7034289 B2	25/04/2006
		US 2006060773 A1	23/03/2006
		US 7223967 B2	29/05/2007
		US 2003153087 A1	14/08/2003
		US 7250306 B2	31/07/2007
		US 2005218320 A1	06/10/2005
		WO 0008454 A1	17/02/2000
		WO 0008455 A1	17/02/2000
		WO 0008456 A1	17/02/2000

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		WO 0008457 A1 WO 03067236 A2 WO 03067237 A2 WO 03067242 A1 WO 03067243 A1 WO 03067244 A2 WO 03067261 A1 WO 03067624 A1 WO 03067625 A1	17/02/2000 14/08/2003 14/08/2003 14/08/2003 14/08/2003 14/08/2003 14/08/2003 14/08/2003 14/08/2003
US 2007023647 A1	01/02/2007	DE 102005031048 A1 GB 0613072 D0 GB 2428872 A GB 2428872 B US 7417224 B2	04/01/2007 09/08/2006 07/02/2007 17/12/2008 26/08/2008
US 2006054804 A1	16/03/2006	AU 2003291523 A1 WO 2004048924 A2	18/06/2004 10/06/2004
WO 02071053 A3	03/01/2003	AT 520145 T AT 553372 T AU 2724401 A AU 6058900 A AU 2002257177 B2 AU 2002306623 A1 AU 2002320210 B2 AU 2003256586 A1 CA 2379502 A1 CA 2403863 A1 CA 2440429 A1 CA 2440429 C CA 2444257 A1 CA 2452128 A1 CA 2493608 A1 CA 2518703 A1 CA 2547389 A1 CA 2550433 A1 CA 2551991 A1 CA 2575556 A1 CN 1390361 A CN 1225006 C CN 1361922 A CN 100358081 C CN 1585666 A CN 1692279 A	15/08/2011 15/04/2012 06/06/2001 13/02/2001 25/11/2004 19/09/2002 22/06/2006 16/02/2004 01/02/2001 17/05/2001 12/09/2002 10/07/2012 24/10/2002 16/01/2003 05/02/2004 23/09/2004 09/06/2005 30/06/2005 28/07/2005 09/02/2006 08/01/2003 26/10/2005 31/07/2002 26/12/2007 23/02/2005 02/11/2005

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
 PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		CN 1692279 B	15/02/2012
		CN 1741244 A	01/03/2006
		EP 1203397 A1	08/05/2002
		EP 1203397 B1	10/08/2011
		EP 1228523 A1	07/08/2002
		EP 1377820 A2	07/01/2004
		EP 1387724 A1	11/02/2004
		EP 1405065 A1	07/04/2004
		EP 1405065 B1	11/04/2012
		EP 1539333 A2	15/06/2005
		EP 1601948 A2	07/12/2005
		EP 1629272 A1	01/03/2006
		EP 1690074 A2	16/08/2006
		EP 1697716 A2	06/09/2006
		EP 1733219 A2	20/12/2006
		EP 1756561 A1	28/02/2007
		EP 1776173 A2	25/04/2007
		EP 1913379 A2	23/04/2008
		EP 1920243 A1	14/05/2008
		EP 1963835 A1	03/09/2008
		EP 2386852 A1	16/11/2011
		GB 0800864 D0	27/02/2008
		GB 2441943 A	19/03/2008
		IL 158386 D0	12/05/2004
		IL 159590 D0	01/06/2004
		JP 2004529461 A	24/09/2004
		JP 4063673 B2	19/03/2008
		JP 2004529467 A	24/09/2004
		JP 4063676 B2	19/03/2008
		JP 2007513340 A	24/05/2007
		JP 4802104 B2	26/10/2011
		JP 2003505846 A	12/02/2003
		JP 5015395 B2	29/08/2012
		JP 2003514349 A	15/04/2003
		JP 2005513414 A	12/05/2005
		JP 2011077054 A	14/04/2011
		JP 2011085604 A	28/04/2011
		JP 2012069531 A	05/04/2012
		US 6495823 B1	17/12/2002
		US 6512224 B1	28/01/2003
		US 2003146377 A1	07/08/2003
		US 6690004 B2	10/02/2004
		US 2003132380 A1	17/07/2003
		US 6806463 B2	19/10/2004
		US 2001030285 A1	18/10/2001
		US 6815668 B2	09/11/2004
		US 6815669 B1	09/11/2004
		US 2004124350 A1	01/07/2004
		US 6972407 B2	06/12/2005

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
 PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		US 2004094704 A1	20/05/2004
		US 7005632 B2	28/02/2006
		US 2005023457 A1	03/02/2005
		US 7030372 B2	18/04/2006
		US 2003052263 A1	20/03/2003
		US 7045776 B2	16/05/2006
		US 2005051719 A1	10/03/2005
		US 7057168 B2	06/06/2006
		US 2005145789 A1	07/07/2005
		US 7075068 B2	11/07/2006
		US 7098449 B1	29/08/2006
		US 2005040330 A1	24/02/2005
		US 7119328 B2	10/10/2006
		US 7122794 B1	17/10/2006
		US 2005133716 A1	23/06/2005
		US 7129482 B2	31/10/2006
		US 2005029449 A1	10/02/2005
		US 7148477 B2	12/12/2006
		US 2006060768 A1	23/03/2006
		US 7157700 B2	02/01/2007
		US 2005017163 A1	27/01/2005
		US 7176453 B2	13/02/2007
		US 2005029443 A1	10/02/2005
		US 7211791 B2	01/05/2007
		US 2005139762 A1	30/06/2005
		US 7227134 B2	05/06/2007
		US 2005156107 A1	21/07/2005
		US 7230238 B2	12/06/2007
		US 2006151687 A1	13/07/2006
		US 7241989 B2	10/07/2007
		US 2006237642 A1	26/10/2006
		US 7262407 B2	28/08/2007
		US 2007045530 A1	01/03/2007
		US 7339164 B2	04/03/2008
		US 2007228269 A1	04/10/2007
		US 7355170 B2	08/04/2008
		US 2005263699 A1	01/12/2005
		US 7365316 B2	29/04/2008
		US 2005253061 A1	17/11/2005
		US 7381944 B2	03/06/2008
		US 2007176092 A1	02/08/2007
		US 7399958 B2	15/07/2008
		US 2006118717 A1	08/06/2006
		US 7435950 B2	14/10/2008
		US 2004240843 A1	02/12/2004
		US 7456390 B2	25/11/2008
		US 2007084999 A1	19/04/2007
		US 7462825 B2	09/12/2008
		US 2006192102 A1	31/08/2006

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
 PCT/FI2013/050440

Patent document cited in search report	Publication date	Patent family members(s)	Publication date
		US 7547879 B2	16/06/2009
		US 2008128609 A1	05/06/2008
		US 7576319 B2	18/08/2009
		US 2009189064 A1	30/07/2009
		US 7579589 B2	25/08/2009
		US 2008121794 A1	29/05/2008
		US 7598489 B2	06/10/2009
		US 2008135745 A1	12/06/2008
		US 7605367 B2	20/10/2009
		US 2007029477 A1	08/02/2007
		US 7608818 B2	27/10/2009
		US 2006255255 A1	16/11/2006
		US 7619214 B2	17/11/2009
		US 2005173629 A1	11/08/2005
		US 7714284 B2	11/05/2010
		US 2012025070 A1	02/02/2012
		US 8410432 B2	02/04/2013
		US 2007252082 A1	01/11/2007
		US 2008128612 A1	05/06/2008
		US 2008185512 A1	07/08/2008
		US 2008224032 A1	18/09/2008
		WO 0108197 A1	01/02/2001
		WO 0135441 A1	17/05/2001
		WO 02083276 A1	24/10/2002
		WO 03005016 A1	16/01/2003
		WO 2004012231 A2	05/02/2004
		WO 2004081527 A2	23/09/2004
		WO 2004092704 A2	28/10/2004
		WO 2004097396 A1	11/11/2004
		WO 2005052546 A2	09/06/2005
		WO 2005059518 A2	30/06/2005
		WO 2005067582 A2	28/07/2005
		WO 2005106450 A1	10/11/2005
		WO 2006015305 A2	09/02/2006
		WO 2006119167 A1	09/11/2006
		WO 2007014303 A2	01/02/2007
		WO 2007056488 A1	18/05/2007

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI2013/050440

CLASSIFICATION OF SUBJECT MATTER

Int.Cl.

G01N 27/62 (2006.01)