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61/667,763 3 July 2012 (03.07.2012) US
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- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).
- Declarations under Rule 4.17:**
- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
 - as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

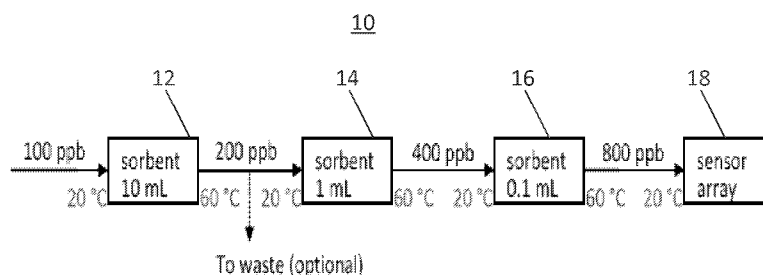
(54) **Title:** DETECTION OF HYDROCARBONS IN AQUEOUS ENVIRONMENTS

FIG. 1

(57) **Abstract:** A process for a pre-concentration unit including: a sorbent material coated passage-way having an entrance for receiving a hydrocarbon-containing groundwater sample and for pre-concentrating the hydrocarbons in a hydrocarbon-containing groundwater sample by successive sorption/desorption cycles, and having an exit for discharging the pre-concentrated hydrocarbons; a heating unit for heating the sorbent material coated passage-way; and; an array of shear horizontal-surface acoustic wave sensors with coatings adapted for detecting and quantifying the pre-concentrated hydrocarbons, disposed at the exit of the sorbent material coated passage-way; and a housing for enclosing the pre-concentration unit and the array of shear horizontal-surface acoustic wave sensors, adapted for continuous use at a body of hydrocarbon-containing groundwater, and coupled to mathematical methods for generating concentrations of specific analytes from both transient and steady-state signals.



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DETECTION OF HYDROCARBONS IN AQUEOUS ENVIRONMENTS

PRIORTITY CLAIM AND CROSS-REFERENCE TO RELATED APPLICATION

5 The present patent application claims priority to United States Patent Application Serial No. 61/667763, filed on July 3, 2012, entitled "System for Detection and Monitoring of Hydrocarbons in Aqueous Environments," which is herein incorporated by reference in its entirety.

10 FIELD OF THE INVENTION

The present invention is directed to a system and process for detection of hydrocarbons in aqueous environments, and more specifically, to pre-concentration and guided shear horizontal-surface acoustic wave sensor-based detection and monitoring of hydrocarbons in
15 aqueous environments.

BACKGROUND OF THE INVENTION

Underground storage tanks ("USTs") for fuel and oil are commonly used, and from time to time may be prone to unintended leakage. Nearly 600,000 federally regulated USTs exist in
20 the United States, and approximately 6,000 leaks are recorded annually as reported by the U.S. Environmental Protection Agency. As such, it is desirable to detect and monitor groundwater in situ in the vicinity of USTs.

Detection of organic compounds can be performed using various sensor technologies, including acoustic-wave, optical and resistive technologies. However, when used without
25 pre-concentration, real-time sensor technologies can detect only some relevant analytes at the required concentration levels, but others are hard to detect, such as benzene which may require detection at levels in the order of 5 ppb (5 µg/L). While sample pre-concentration in the gas phase is a well known, a need remains for pre-concentration of volatile organic compounds in the aqueous phase.

30 Sensors are known for determining benzene concentrations at low levels in the gas phase, but not in water. The use of traditional analysis methods requires technicians to visit the field, preserve the samples and then ship samples to a lab. Typically, results for these traditional

analyses are not reported for two or more weeks. An improved method of monitoring dissolved hydrocarbons in groundwater is desired.

SUMMARY OF THE INVENTION

5 The present integrated system and process is directed to a pre-concentrator and guided shear horizontal-surface acoustic wave (“SH-SAW”) device for sensor-based detection and monitoring of hydrocarbons in aqueous environments. This new on-site detection and monitoring system seeks to generate results for analytes of interest.

In one embodiment, the invention is a device including a pre-concentration unit comprising:
10 a passage-way containing a sorbent material with an entrance for receiving a hydrocarbon-containing groundwater sample and for pre-concentrating the hydrocarbons in a hydrocarbon-containing groundwater sample by single or successive iterative sorption/desorption cycles, and having an exit for discharging the pre-concentrated hydrocarbons; a heating unit for heating the passage-way containing a sorbent material; and
15 an array of shear horizontal – surface acoustic wave sensors with coatings adapted for detecting and quantifying the pre-concentrated hydrocarbons, disposed at the exit of the sorbent material coated passage-way; and a housing for enclosing the pre-concentration unit and the array of shear horizontal – surface acoustic wave sensors, adapted for continuous use in a body of hydrocarbon-containing groundwater.

20 This invention will include the use of mathematical methods to predict the steady-state response from the transient signals well before equilibrium as well as deconvolve the signal to generate concentration values for the analytes of interest.

In another embodiment, the invention is a method of on-site detection of hydrocarbons in groundwater using the device of the invention.

25 BRIEF DESCRIPTION OF THE DRAWINGS

The drawings are not necessarily to scale or exhaustive. Instead, emphasis is generally placed upon illustrating the principles of the inventions described herein. The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate several embodiments consistent with the disclosure and together with the description, serve
30 to explain the principles of the disclosure. In the drawings:

FIG. 1 is a flow diagram of a process for detecting hydrocarbons in aqueous environments in accordance with an embodiment of the present invention.

FIG. 2 is a block diagram of a system for detecting hydrocarbons in aqueous environments in accordance with an embodiment of the present invention.

5 FIG. 3 is an illustration of an assembled cylindrical pre-concentration unit in accordance with an embodiment of the present invention.

FIG. 4 is an illustration of an assembled planar pre-concentration unit in accordance with an embodiment of the present invention.

10 FIG. 5 is an illustration of an exemplary serpentine flow path for a planar pre-concentration unit in accordance with an embodiment of the present invention.

FIG. 6 is an illustration of an exemplary bifurcated flow path for a planar pre-concentration unit in accordance with an embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The following detailed description refers to the accompanying drawings. Wherever possible,
15 the same reference numbers are used in the drawings and the description to refer to the same or similar parts. Also, similarly-named elements may perform similar functions and may be similarly designed, unless specified otherwise. Numerous details are set forth to provide an understanding of the described embodiments. The embodiments may be practiced without these details. In other instances, well-known methods, procedures, and components have not
20 been described in detail to avoid obscuring the described embodiments. While several exemplary embodiments and features are described here, modifications, adaptations, and other implementations may be possible, without departing from the spirit and scope of the invention. Accordingly, unless stated otherwise, the descriptions relate to one or more embodiments and should not be construed to limit the invention as a whole. Instead, the
25 proper scope of the invention is defined by the appended claims.

The present invention relates to a system and method for detecting and monitoring comprised of a pre-concentration unit and acoustic-wave devices based detection for volatile organic compounds directly in the aqueous phase. The invention is intended to be suitable for

implementation in existing groundwater monitoring wells as they exist at numerous locations, such as UST sites, refineries and terminals.

In one embodiment, the invention includes a pre-concentration unit having a substrate and sorbent material which sorbs organic compounds from a water sample, which will then be released when heated to a specific temperature. Since aqueous phases do not permit excessive heating, the pre-concentration unit in one embodiment is a multi-step system. The pre-concentrated sample is then detected in an array of SH-SAW sensors with various coatings. By evaluating both steady-state signal shift and time dependence of response (known as the transient response), one or several organic compounds present in the sample can be detected and quantified.

The invention includes a pre-concentration unit (which can be a multi-step system) and an array of acoustic-wave based sensors for selective detection and quantification of volatile organic compounds in-situ in the aqueous phase. A non-limiting example of the multi-step system is shown in FIG. 1. FIG. 1 shows a hypothetical example of how an aqueous sample is successively exposed to sorbent materials and heated to perform the pre-concentration.

FIG. 2 is a block diagram of a system 20 for in situ detection in groundwater in accordance with an embodiment of the present invention. The solid black arrows show the flow of liquid containing the hydrocarbons to be analyzed, and the dashed black arrows show the direction of information and control. In accordance with the system shown in FIG. 2, an aqueous sample 21 is optionally diverted through a particulate filter 22 to remove undesired particulates from the aqueous sample to be analyzed. The sample is then pumped via fluid pump 23 to a pre-concentrator unit 24 that performs a successive or "iterative" pre-concentration process as described with reference to FIG. 1. In the pre-concentration unit 24, the aqueous sample (filtered or unfiltered) is collected, gathered or otherwise contained within or in communication with a first sample collector at ambient temperature. The sample collector 24 is preferably constructed of a first sorbent material, and is optionally coupled to a particulate filter (not shown) for removing undesired particulates from the aqueous sample.

After a suitable collection time, which duration may depend on the compound to be analyzed, a heater will heat the sample to promote the release of sorbed analytes from sample collector 24. If a still higher concentration ratio is desired, such pre-concentrated sample is then pumped to a second sorbent phase where the pre-concentration process is repeated, etc. The

indicated concentrations (in ppb = $\mu\text{g/L}$) in FIG. 1 schematically show how the concentration of an analyte in the sample might increase with each pre-concentration step (exact concentration values are arbitrary, as are the temperatures and volumes of the various sorbent phases shown). Alternatively, a higher concentration ratio can be achieved in a more continuous form, where a heated zone is passing through a pre-concentration unit with the same velocity as a simultaneously pumped sample; the concentration of volatile hydrocarbons in the sample will then continuously increase as the latter is proceeding through the pre-concentration unit (not shown). At the end of the multi-step system, the pre-concentrated sample will be detected in a sensor array which, e.g., might consist of multiple SH-SAW (shear-horizontal surface acoustic wave) sensors with different coatings, which will sorb the relevant analytes from the sample and induce a response signal in the sensors.

In accordance with one non-limiting embodiment of the present invention, the pre-concentration unit (or pre-concentrator) includes a flow path through a selected sorbent material that exposes organic analyte in aqueous solution to a selective coating, favors sorption of the analyte, which is subsequently desorbed via thermal release (heating). General design parameters for the pre-concentration unit include: (1) the capacity of pre-concentration (e.g., chemistry of selective coating, thickness of coating, coating on a substrate filler, such as beads, and flow path length, total amount of coating material); and (2) the efficiency of heat transfer for release (e.g., material the device is made of, thickness of the material, exposure to heat; such as areas that heat is applied and cross sectional area of flow path, and flow rate).

The coating is a chemical species that must be effective in both the sorption and (thermally induced) desorption of the analyte of interest in comparison to other analytes in the aqueous phase. The amount or mass of coating material relates to the size of the concentrated fluid volume released; more coated material will result in a larger sample volume for the detector to measure. In order to optimize sorption and desorption, a thinner film (a few microns or less) is favorable, with larger surface area, hence coating on a support substrate (polymer or glass beads, or glass fibers are examples).

The thermal release of sorbed analyte can be achieved by applying resistive heating. Metal wires or patterned metal films can be used to generate heat. Heating wire is more convenient to use with a cylindrical configuration (see for example FIG. 3) because it can be more easily

wrapped around the exterior of tubing, than a flat heater pad. Planar configurations (see for example FIG. 4) can take advantage of flat pre-manufactured heating pads. The option also exists to integrate heating elements into a planar device if fabrication techniques for miniaturization are used, such as depositing thin metal films by evaporation. With heating elements integrated into the device, very precise heating is possible, to minimize power consumption and maximize efficiency. One additional consideration is that the heating needs to warm the aqueous phase without boiling or causing a gas phase to develop, therefore temperature sensors and a heating controller are needed.

Referring now to FIGS. 3 and 4, the pre-concentration units may be cylindrical or planar. A cylindrical design is typically more convenient to assemble due to readily available connections and tubing; planar designs, however, have the potential for more dense fluidic channels and more efficient heating, which may result in more efficient pre-concentration

FIG. 3 shows a finally-assembled cylindrical pre-concentration unit 36 in accordance with an embodiment of the present invention. Solid black arrows show the flow of the liquid. The pre-concentration unit 36 includes a passageway (or conduit) 32 and a heater element 34. The heater element 34 can be in the form of a coil that is in communication with the conduit 32 so as to enable heat transfer and cause heating of the conduit 32 and thus heating of the aqueous sample passing therethrough. The coil can be heated, for example, via an electrical source coupled to leads 35a and 35b.

Cylindrical flow paths can be constructed using commonplace tubing materials, such as metal tubing (copper or stainless steel), polymer plastic (PTFE, PET, PEEK...etc.), or glass. Because of the inherent symmetry of such materials, the radius is constant and a circular cross section exists. When using machining or semiconductor fabrication techniques to form the flow path, the shape will be rectangular or trapezoidal. Depending on the aspect ratio (defined as the ratio of height to width) of the cross sectional area, both shallow and wide (low aspect ratio) or tall and narrow (high aspect ratio) flow paths may be formed. While physical flow properties are similar in non-cylindrical versus cylindrical flow paths, some differences exist, and may need to be considered when understanding device performance.

FIG. 4 shows a finally-assembled planar pre-concentration unit 48 in accordance with an embodiment of the present invention. The planar pre-concentration unit 48 includes a top

plate 42 with fluid/tubing connectors 43a and 43b, a bottom plate 44 with fluid flow path (including coating) 45, and a heater pad 46 for bottom plate 44. Connections 43a and 43b can be machined from metal, or made of plastic materials and attached to the top plate 42 with an epoxy. Leads 47a and 47b are provided for coupling the heater pad 46 to an electrical source. Components 42-48 can be “sandwich” stacked and held together with bolts, epoxy or other means (not shown) to form the finally-assembled planar pre-concentration unit 48.

Optionally, a chemically inert O-ring, flat gasket or other sealing component can be arranged between the top plate 42 and bottom plate 44 to prevent leakage of fluid from the flow path 45.

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Planar configurations are advantageous for miniaturization: commercial fabrication techniques used to manufacture small features are designed for planar formats. Heating is easier to achieve as well, due to the large flat surface area, and thin material thickness (favoring rapid heating), with the heating element only needing attachment in two dimensions (cylindrical needs three, for the curved surface) which makes the device more durable than cylindrical tubing. Planar configuration is also amenable to stacking, if more than one concentration stage is desired.

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FIG. 5 shows an exemplary, non-limiting flow path 45 for a planar pre-concentrator unit. As shown in FIG. 5, a serpentine channel of bifurcated grooves can be used as a configuration for the flow path. Alternatively, a bifurcated design as shown in FIG. 6 may be advantageous and less prone to the effects of clogging. With a bifurcated design 65, the entrance channel is split into two channels, those two split into two, etc., then reversed (two combines to one) to result in one channel leaving the device. The bifurcated design 65 is less sensitive to clogging: if a clog occurs in the split channels, flow continues in the other parallel channels. It is also less demanding on pumps and easier to machine. The bifurcated design, however, does not have the ability to create as dense features as the serpentine design. Feature density is a consideration, where increasing feature density results in an increase in concentrated sample volume.

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In accordance with another embodiment, the top and bottom plates of a planar device can be fabricated from brass, aluminum, stainless steel and other metals that are favorable for efficient conduction of heat. However, challenges arise when attempting to use conventional

machining methods for small flow path dimensions (<800 microns). For miniaturization on the scale of tens to hundreds of microns, semiconductor fabrication methods are available, and common substrates are silicon and glass. Semiconductor methods also provide the option for integrating heating systems or selective coatings. Polymer materials are possible but less desirable due to poor thermal conduction and some machining limitations.

The heating device used with the planar pre-concentration device is a metal film heater: this was chosen because of the efficiency of design (it can apply heating to a large area without adding bulk to the device). The heat element is applied to the thinner of the metal plates (the plate with the fluid channels) because the thin metal walls will transfer the heat more efficiently (due to reduced thermal mass) to the aqueous phase to desorb the concentrated analyte. The thin heater is also beneficial in that it can quickly reach temperature (on the order of seconds) and consequently heat the liquid phase (on the order of a minute).

What has been described above includes examples of the present invention. It is, of course, not possible to describe every conceivable combination of components or methodologies for purposes of describing the present invention, but one of ordinary skill in the art may recognize that many further combinations and permutations of the present invention are possible. Accordingly, the present invention is intended to embrace all such alterations, modifications and variations that fall within the spirit and scope of the appended claims. Furthermore, to the extent that the term "includes" is used in either the detailed description or the claims, such term is intended to be inclusive in a manner similar to the term "comprising" as that term is interpreted as a transitional word in a claim.

WHAT IS CLAIMED IS:

1. A system for in situ monitoring of groundwater, comprising:
 - a. a pre-concentration unit comprising:
 - 5 a sorbent material coated passage-way having an entrance for receiving a sample of the groundwater containing a hydrocarbon and for pre-concentrating the hydrocarbon contained in the sample by successive sorption/desorption cycles, and having an exit for discharging the pre-concentrated hydrocarbon; and
 - a heating unit for heating the sorbent material coated passage-way;
 - 10 b. an array of shear horizontal-surface acoustic wave sensors with coatings adapted for detecting and quantifying the pre-concentrated hydrocarbon, disposed at the exit of the sorbent material coated passage-way of the pre-concentration unit; and
 - c. a housing for enclosing the pre-concentration unit and the array of shear horizontal-surface acoustic wave sensors.
- 15 2. The system according to claim 1, wherein the housing is adapted for continuous use at a body of hydrocarbon-containing groundwater.
3. The system according to claim 1, wherein the output of the device indicates the species and concentrations of one or more hydrocarbons in the groundwater sample.
4. The system according to claim 1, further comprising a computer processor in
20 communication with the acoustic wave sensors, the processor configured to receive signals for the acoustic wave sensors and to execute a computer executable code responsive to the signals, the computer executable code comprising code for calculating an equilibrium concentration corresponding to a specific analyte.
5. The system according to claim 1, further comprising a controller in communication
25 with the heating unit for controlling the heating of the sorbent material coated passage-way.
6. The system according to claim 1, wherein the pre-concentration unit is a cylindrical pre-concentration unit.

7. The system according to claim 1, wherein the pre-concentration unit is a planar pre-concentration unit.

8. The system according to claim 1, wherein the planar pre-concentration unit comprises a serpentine passage-way.

5 9. The system according to claim 1, wherein the planar pre-concentration unit comprises a bifurcated passage-way.

10. A method for in situ monitoring of groundwater, comprising passing sample of the groundwater containing a hydrocarbon to a device comprising a pre-concentration unit comprising a sorbent material coated passage-way having an entrance for receiving the and
10 for pre-concentrating the hydrocarbon by successive sorption/desorption cycles, and having an exit for discharging the pre-concentrated hydrocarbon; and a heating unit for heating the sorbent material coated passage-way; and an array of shear horizontal – surface acoustic wave sensors with coatings adapted for detecting and quantifying the pre-concentrated hydrocarbon, disposed at the exit of the sorbent material coated passage-way; and a housing
15 for enclosing the pre-concentration unit and the array of shear horizontal-surface acoustic wave sensors; and wherein the output of the device indicates the species and concentration of hydrocarbons in the hydrocarbon-containing groundwater sample.

11. A method for quantification of hydrocarbons using estimation theory that allows the equilibrium concentrations to be calculated for specific analytes from the initial stages of the
20 transient response.

12. A pre-concentration device, comprising:

- a. an inlet for accepting an aqueous sample containing a hydrocarbon compound to be detected;
- b. a plurality of conduits, each comprising a respective sorbent material and
25 heater element, arranged serially so as to pre-concentrate the hydrocarbon contained in the sample by successive sorption/desorption cycles.

13. The device according to claim 12, comprising an outlet for discharging the pre-concentrated hydrocarbon.

14. The device according to claim 12, wherein at least one of the conduits is cylindrical.
15. The device according to claim 12, wherein at least one of the conduits is planar.
16. The device according to claim 12, wherein the planar pre-concentration unit includes a serpentine conduit.
- 5 17. The device according to claim 12, wherein the planar pre-concentration unit includes a bifurcated conduit.

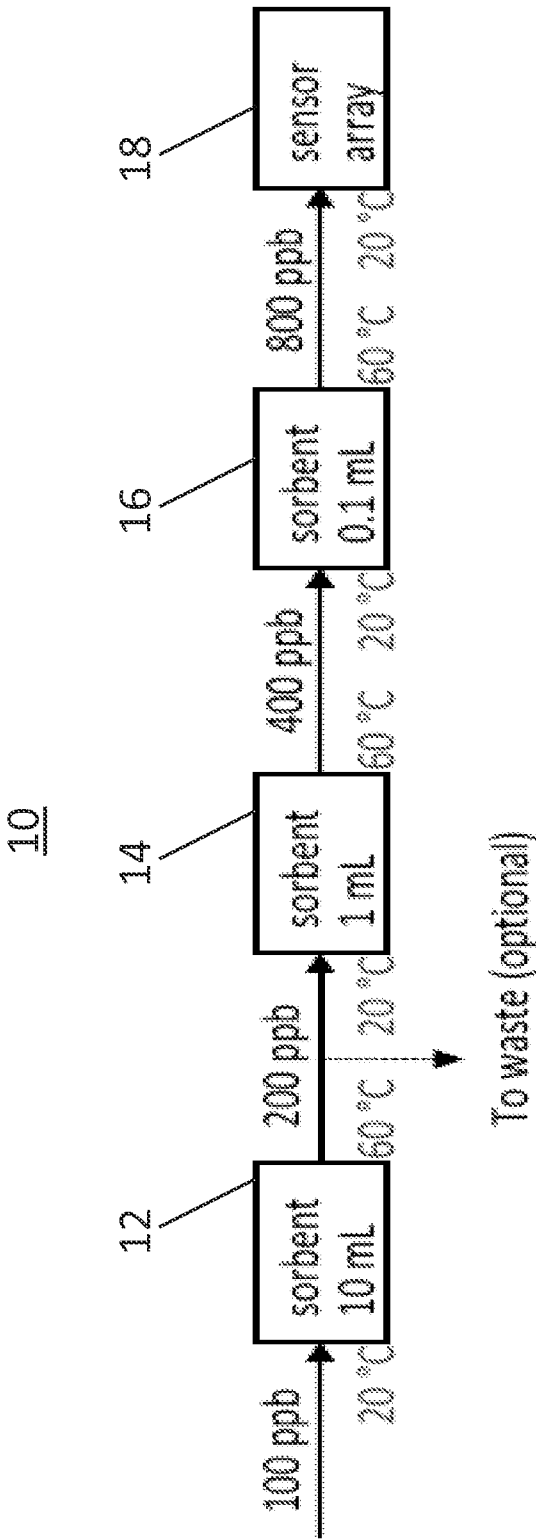


FIG. 1

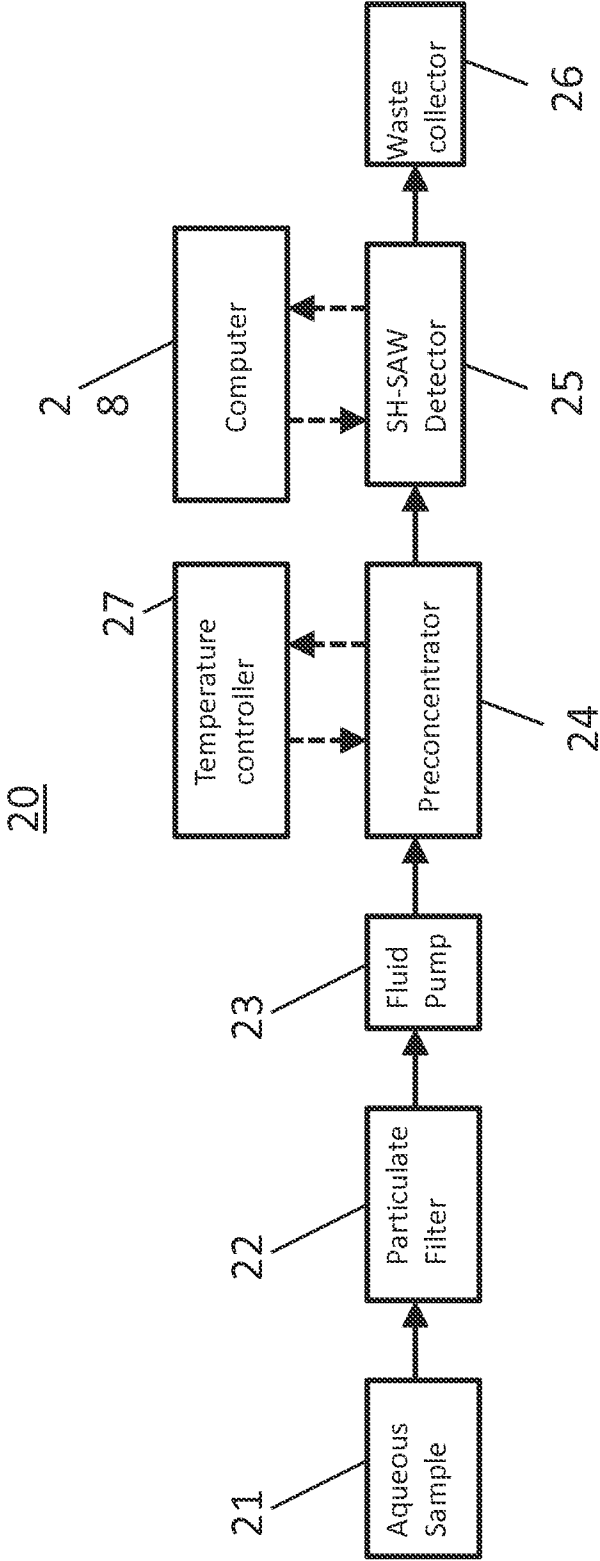


FIG. 2

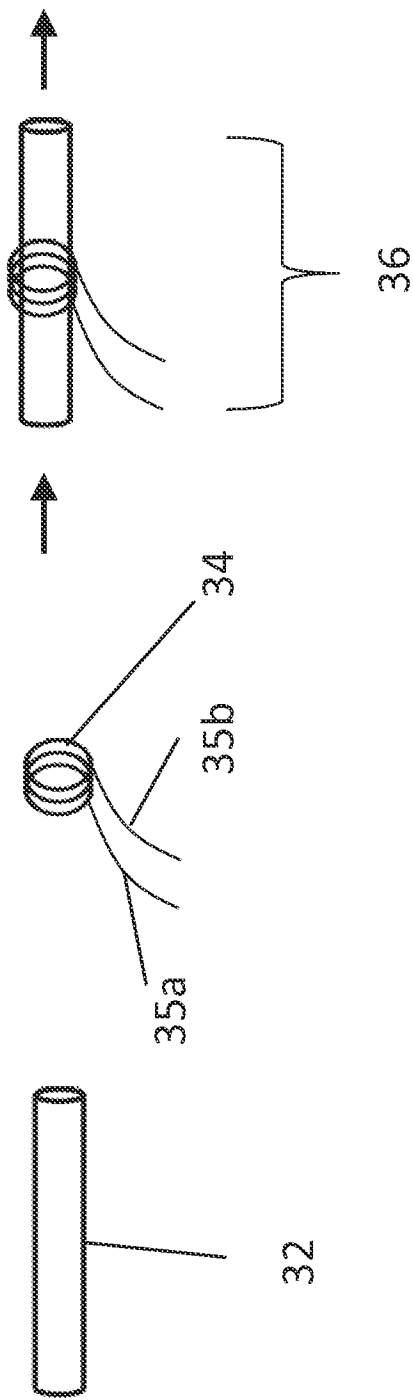


FIG. 3

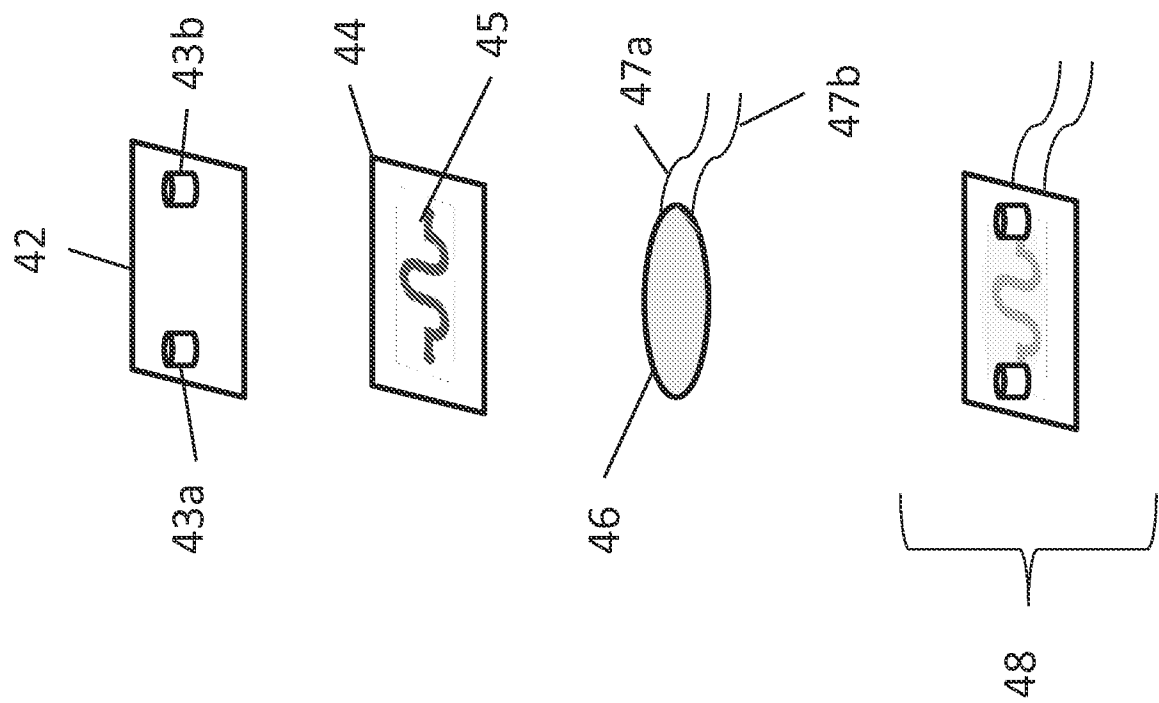


FIG. 4

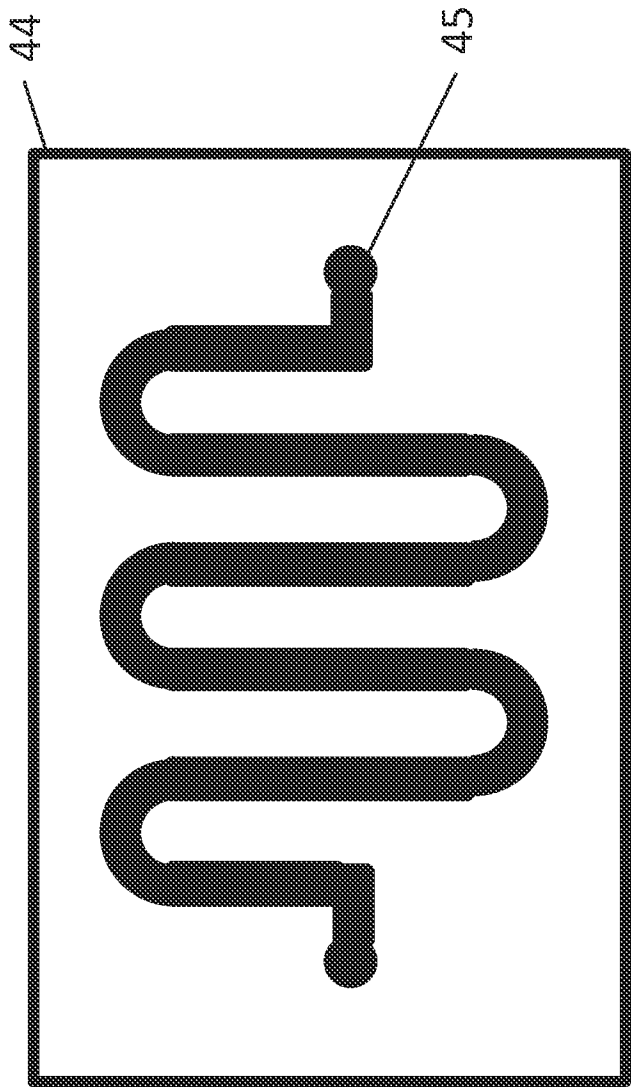


FIG. 5

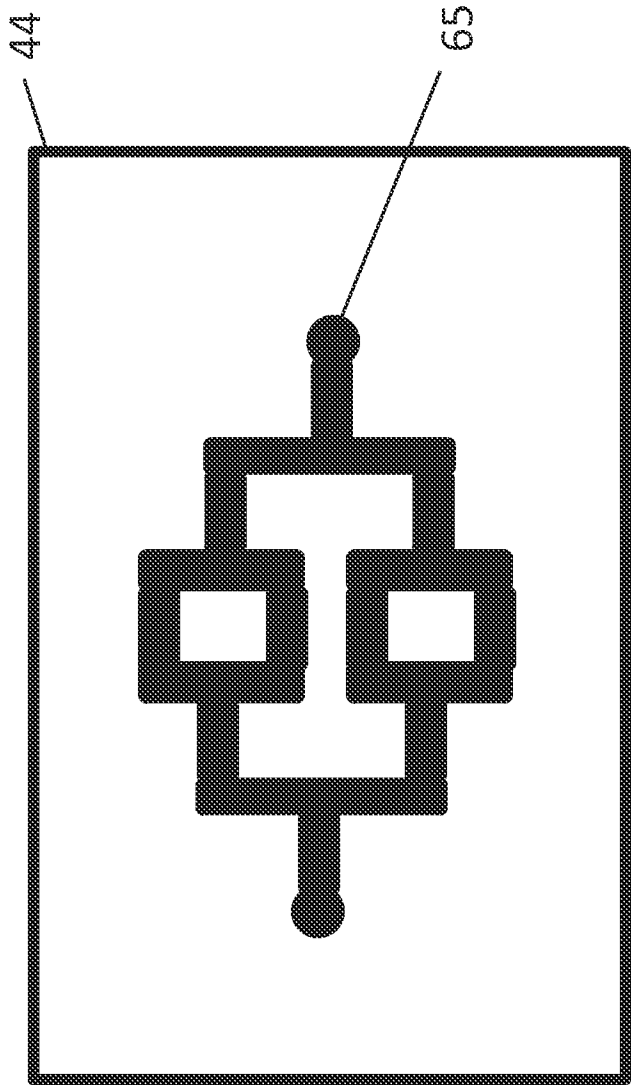


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/049185

A. CLASSIFICATION OF SUBJECT MATTER
INV. G01N29/02 G01N1/40 G01N33/18
ADD.

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)
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 practicable, search terms used)

EPO-Internal, WPI Data, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/289397 A1 (HASSAN KAZI ZULFIQUR ALI [US] ET AL ALI HASSAN KAZI ZULFIQUR [US] ET A) 27 November 2008 (2008-11-27)	1-5,7-10
Y	abstract; figures 1,2, 6-13 paragraphs [0009] - [0026], [0042] - [0072]	6
X	----- WO 99/66304 A1 (CALIFORNIA INST OF TECHN [US]; CYRANO SCIENCES INC [US]; LEWIS NATHAN) 23 December 1999 (1999-12-23) abstract; figures 1,2 page 4, line 5 - line 26 page 18, line 10 - line 18	1,10
X	----- US 2005/065446 A1 (TALTON JAMES D [US]) 24 March 2005 (2005-03-24) abstract; figures 1A-3 paragraphs [0026], [0045], [0052] ----- -/-	1,10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent 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

2 October 2013

Date of mailing of the international search report

04/11/2013

Name and mailing address of the ISA/

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Authorized officer

Uttenthaler, Erich

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/049185

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 11-17
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2013/049185

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2008/148815 A1 (LUCAS JONATHAN DAY [US] ET AL) 26 June 2008 (2008-06-26) abstract; figures 1A-5 paragraphs [0038] - [0058] -----	6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2013/049185

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2008289397	A1	27-11-2008	NONE

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FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

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The search has been restricted to the subject-matter indicated by the applicant in his letter of 30.08.13, i.e. claims 1-9, filed in reply to the invitation to indicate the apparatus and the method claim on which a search is to be carried out with letter from 20.08.2013.

Additionally
method claim 10 will also be searched since the subject matter corresponds, mutatis mutandis, to the apparatus claim 1.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.