

A METHOD OF MEASURING VOLATILE ORGANIC COMPOUNDS

Technical Field

5 The present invention relates to a method for measuring the amount of volatile organic compounds and/or identifying a target volatile organic compound in a sample. There are also provided systems for carrying out the method.

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Background

Volatile organic compounds (VOCs) belong to a subset of organic compounds with inherent physical and chemical properties that allow them to move between water and air.

15 In general, VOCs have high vapor pressures, low-to-medium solubilities in water, and low molecular weights in comparison with other types of organic compounds. Some VOCs may occur naturally in the environment. While other VOCs occur only as a result of man-made activities,

20 others originate from both sources. Examples of VOCs include formaldehyde, trichloroethane, bromodichloromethane and carbon tetrachloride.

There is growing concern regarding the quality of natural

25 and treated water supplies, which are susceptible to contamination by both natural and anthropogenic chemical sources. The contamination of these water supplies by VOCs is of particular concern because these compounds potentially can cause significant health effects such as

30 liver or nervous system problems, reproductive anomalies, and increased risks of cancer.

A variety of removal and detection methods have been used in the analysis of water samples to determine the

presence of VOCs. Most of the removal methods are based on stripping of the VOCs present in the sample, and pervaporation techniques.

5 In the earlier technique mentioned, an inert gas is used to sparge the VOCs from the sample into the gas phase before subjecting the VOCs to a suitable detection method. A variation of this occurs in the introduction of a suitable adsorbent to contain the sparged VOCs before
10 inducing the desorption of the VOC into a detection system. In the sparging technique, the presence of a mixture of VOCs in a sample presents a large range of solubility values in a sample. Non-polar VOCs such as halogenated hydrocarbons and aromatic hydrocarbons can be
15 easily stripped off, while polar compounds like alcohols, ketones, esters, ethers, nitriles and thiols form azeotropic mixtures with water and meet with limited success to be sparged out from a sample. It is possible to introduce a heating process or a longer sparging time
20 to improve the extent and efficiency of sparging polar compounds in azeotropic mixtures. However, safety issues related to the flammability of the VOCs, and/or delays/inaccuracies in the downstream detection of the VOCs are of concern in the use of such heating processes
25 or extended sparging times.

The other commonly used pervaporation technique targets mostly hydrophobic VOCs and therefore cannot be suitably adapted to a sample containing a wide range of VOCs.

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In general, downstream detection methods to one of the sparging or pervaporation techniques are based on the use of catalytic oxidation followed by non-dispersive infrared (NDIR) detection methods. Gas and liquid

chromatography with a mass spectrometer can also be used but these methods usually rely on labor-intensive sample collection/laboratory-based analysis, thereby posing limitations to the frequency of collection and analyses of samples. In addition, where offsite analyses of samples are required, the integrity of the collected samples may be compromised during the conduct of sample collection, transportation and storage.

Accordingly, there is a need to provide a new monitoring and detection method for VOCs that overcomes or at least ameliorates the disadvantages described above, such that in-situ VOC monitoring which is sensitive, extensive, compact, and offers low power consumption may be used in long-term monitoring applications.

Summary

In a first aspect, there is provided a method of quantifying the total amount of VOCs in a sample comprising the steps of:

- (a) providing a feed stream of polar and non-polar VOCs in a liquid phase;
- (b) separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;
- (c) passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and
- (d) measuring the quantity of VOCs in the volatile phase of step (b) and the permeate stream of step (c) to calculate the total amount of VOCs in said sample.

In a second aspect, there is provided a method of identifying targeted VOCs present in a sample, comprising the steps of:

(a) providing a feed stream of polar and non-polar VOCs
5 in a liquid phase;

(b) separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;

(c) passing the liquid phase through a permeable barrier
10 to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and

(d) analyzing the VOCs in the volatile phase of step (b) and the permeate stream of step (c) to thereby identify said targeted VOCs in said sample.

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In a third aspect, there is provided a system to quantify the total amount of VOCs in a sample comprising the following:

(a) means of providing a feed stream of polar and non-
20 polar VOCs in a liquid phase;

(b) means of separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;

(c) means of passing the liquid phase through a permeable
25 barrier to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and

(d) means of measuring the quantity of VOC in the volatile phase of step (b) and the permeate stream of step (c) to calculate the total amount of VOCs in said
30 sample.

In a fourth aspect, there is provided a system to identify targeted VOCs comprising the following:

(a) means of providing a feed stream of polar and non-polar VOCs in a liquid phase;

5 (b) means of separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;

(c) means of passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC
10 permeate stream and non-VOC retentate stream; and

(d) means of analyzing the VOCs in the volatile phase of step (b) and the permeate stream of step (c) to thereby identify said targeted VOCs in said sample.

15 Advantageously, the disclosed method of quantifying the total amount of VOCs in a sample allows for the implementation of the separating step in series before the step of passing the liquid phase through a permeable barrier, thereby allowing essentially for all non-polar
20 VOCs to be separated from the feed stream before allowing essentially for all polar VOCs to be separated from the liquid phase. The inventor has found that if the separating step is after the passing step, some of the non-polar VOCs may be lost, leading to an inaccuracy in
25 the total amount of VOCs that can be measured. Hence, it is essential that the separating step is before the passing step so that substantially all the non-polar VOCs and polar VOCs can be captured and measured.

30 Advantageously, the disclosed method of identifying targeted VOCs present in a sample allows for the implementation of the separating step in series before

the step of passing the liquid phase through a permeable barrier, thereby allowing essentially for all non-polar VOCs to be separated from the feed stream before allowing essentially for all polar VOCs to be separated from the
5 liquid phase.

Advantageously, the disclosed method of quantifying the total amount of VOCs in a sample provides a method which is capable of detecting and accounting for a wide range
10 of VOCs, including polar or non-polar compounds and hydrophobic or hydrophilic compounds.

Further advantageously, the current disclosure also allows for the identification of a targeted VOCs in a
15 sample in addition to the measurement of the total content of the VOCs within the sample.

Even further advantageously, the method may be incorporated into a mobile system which allows the on-
20 site sampling and analysis of VOCs, eliminating concerns with regard to maintaining the integrity of the samples in the process of transporting and storing the samples.

25 **Definitions**

The following words and terms used herein shall have the meaning indicated:

The term "volatile" when used in describing an organic
30 compound, refers to an organic compound with a boiling

point of less than or equal to 250°C when measured at standard conditions.

5 The words "predominantly", "essentially" and "substantially" do not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention.

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Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit
15 inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more
20 typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

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Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and brevity and should not be construed as an inflexible
30 limitation on the scope of the disclosed ranges.

Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical

values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

10 **Disclosure of Optional Embodiments**

Exemplary, non-limiting embodiments of a method for measuring the amount of volatile organic compounds and/or identifying a target volatile organic compound in a sample will now be disclosed.

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The method of quantifying the total amount of VOCs in a sample comprises the steps of:

- (a) providing a feed stream of polar and non-polar VOCs in a liquid phase;
- 20 (b) separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;
- (c) passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non- VOC retentate stream; and
- 25 (d) measuring the quantity of VOCs in the volatile phase of step (b) and the permeate stream of step (c) to calculate the total amount of VOCs in said sample.

30 The method of identifying targeted VOCs present in a sample, comprises the steps of:

- (a) providing a feed stream of polar and non-polar VOCs in a liquid phase;
- (b) separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase
5 that predominantly contains polar VOCs;
- (c) passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and
- (d) analyzing the VOCs in the volatile phase of step (b)
10 and the permeate stream of step (c) to thereby identify said targeted VOCs in said sample.

The VOCs within the sample to be quantified or identified are not limited and may be selected from the group
15 consisting of dichloroacetonitrile, chloroform, iodobenzene, 1,1,2-trichlorotrifluoroethane, trichloroethylene, perchloroethylene, carbon tetrachloride, chloroform, 1,1-dichloroethene, vinyl chloride, trans-1, 2-dichloroethene, cis-1, 2-
20 dichloroethene, dichloromethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane, bromoform, bromodichloromethane and chlorodibromomethane, ethanol, acetone, acetic acid, isopropyl alcohol (IPA), dichloromethane, hexane, ethyl acetate, toluene, butyl
25 acetate, benzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, xylene, chlorobenzene, ethylbenzene and 2-propenamide.

The sample may be in the form of groundwater, riverine
30 water, reservoir water, tap water, wastewater and potable drinking water. The sample prior to treatment may contain up to 50% solids which may be removed by a process comprising centrifugation, filtration, sedimentation,

coagulation or flocculation. The composition of the sample prior to treatment may be made up of about 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.06%, 0.07%, 0.08%, 0.09%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 20%, 30%, 30%, 40% or 50% solids.

The step of separating the feed stream may comprise the step of gas stripping the sample with a suitable gas. The gas stripping of the VOCs may involve the use of a purge gas. The purge gas may be N₂, H₂, Ar, O₂, Kr, Xe, or ambient air. The purge gas used in the stripping step may be subjected to a flowrate of about 50 mL/min to about 10 L/min.

The step of separating the feed stream may be carried out prior to the step of passing the liquid phase through a permeable barrier, and in series with it. The step of separating the feed stream may also be carried out in parallel to the step of passing the liquid phase through a permeable barrier.

The permeable barrier may contain a plurality of membranes. The membranes used may either be ultrafiltration or nanofiltration membranes. The membrane module may be in the form of flat sheets, hollow fibers, tubes and spiral wound structures arranged in parallel or in series. The membrane module may comprise a polymeric or ceramic material. The polymeric material may be one of the following: cellulose acetate (CA), nitrocellulose (CN), cellulose esters (CE), polysulfone (PS), polyether sulfone (PES), polyacrylonitrile (PAN), polyamide, polyimide, polyethylene (PE), polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidene fluoride

(PVDF) or polyvinylchloride (PVC). The ceramic material may be one of the following: alumina, zirconia, titania or silicon carbide.

5 The membrane module may have a molecular weight cut-off of 1×10^6 Da, 1×10^5 Da, 1×10^4 Da, 1×10^3 Da or 1×10^2 Da. The membrane module may be of an average pore size of 0.001 μm , 0.002 μm , 0.003 μm , 0.004 μm , 0.005 μm , 0.006 μm , 0.007 μm , 0.008 μm , 0.009 μm , 0.01 μm , 0.02 μm ,
10 0.03 μm , 0.04 μm , 0.05 μm , 0.06 μm , 0.07 μm , 0.08 μm , 0.09 μm or 0.1 μm .

The membrane module may be operated at a transmembrane gauge pressure of about 1 bar to about 10 bars.

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The step of measuring the quantity of VOCs may be carried out with a total organic carbon analyzer. The total organic carbon analyzer may also include a suitable chamber for the measurement of inorganic carbon content.

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The step of analyzing the VOCs may be carried out using an NDIR detector, a dry electrolytic conductivity detector, a thermionic ionization detector, a flame ionization detector, a thermally conductivity detector or
25 an electron capture detector. Hence the total amount of VOCs present in the sample may be quantitatively measured.

Exemplary, non-limiting embodiments of a system to
30 quantify the total amount of VOCs and/or to identify targeted VOCs in a sample will now be disclosed.

The system to quantify the total amount of VOCs in a sample comprises the following:

- (a) means of providing a feed stream of polar and non-polar VOCs in a liquid phase;
- (b) means of separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;
- (c) means of passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non- VOC retentate stream; and
- (d) means of measuring the quantity of VOCs in the volatile phase of step (b) and the permeate stream of step (c) to calculate the total amount of VOCs in said sample.

The system to identify targeted VOCs comprises the following:

- (a) means of providing a feed stream of polar and non-polar VOCs in a liquid phase;
- (b) means of separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;
- (c) means of passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and
- (d) means of analyzing the VOCs in the volatile phase of step (b) and the permeate stream of step (c) to thereby identify said targeted VOCs in said sample.

The VOCs to be detected or identified in the sample are not limited and may be selected from the group consisting of dichloroacetonitrile, chloroform, iodobenzene, 1,1,2-trichlorotrifluoroethane, trichloroethylene,

perchloroethylene, carbon tetrachloride, chloroform, 1,1-dichloroethene, vinyl chloride, trans-1, 2-dichloroethene, cis-1, 2-dichloroethene, dichloromethane, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,2-dichloroethane, bromoform, bromodichloromethane and chlorodibromomethane, ethanol, acetone, acetic acid, isopropyl alcohol (IPA), dichloromethane, hexane, ethyl acetate, toluene, butyl acetate, benzene, 1,2,4-trichlorobenzene, 1,4-dichlorobenzene, 1,2-dichlorobenzene, xylene, chlorobenzene, ethylbenzene and 2-propenamide.

The sample may be in the form of groundwater, riverine water, reservoir water, tap water, wastewater and potable drinking water. The sample prior to treatment may contain up to 50% solids which may be removed by a process comprising centrifugation, filtration, sedimentation, coagulation or flocculation. The composition of the sample prior to treatment may be made up of about 0.01%, 0.02%, 0.03%, 0.04%, 0.05%, 0.06%, 0.07%, 0.08%, 0.09%, 0.1%, 0.2%, 0.3%, 0.4%, 0.5%, 0.6%, 0.7%, 0.8%, 0.9%, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, 20%, 30%, 30%, 40% or 50% solids.

The means of separating the feed stream may comprise the use of a gas stripper with a suitable purge gas. The gas may be N₂, H₂, Ar, O₂, Kr, Xe, or ambient air. The purge gas used in the stripping step may be subjected to a flowrate of about 50 mL/min to about 10 L/min.

The means of separating the feed stream may be implemented prior to the means of passing the liquid phase through a permeable barrier, and in series with it. The means of separating the feed stream may also be

implemented in parallel to the means of passing the liquid phase through a permeable barrier.

5 The permeable barrier may contain a plurality of membranes. The membranes used may either be ultrafiltration or nanofiltration membranes. The membrane module may be in the form of flat sheets, hollow fibers, tubes and spiral wound structures arranged in parallel or in series. The membrane module may comprise a polymeric or ceramic material. The polymeric material may be one of the following: cellulose acetate (CA), nitrocellulose (CN), cellulose esters (CE), polysulfone (PS), polyether sulfone (PES), polyacrylonitrile (PAN), polyamide, polyimide, polyethylene (PE), polypropylene (PP), 15 polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) or polyvinylchloride (PVC). The ceramic material may be one of the following: alumina, zirconia, titania or silicon carbide.

20 The membrane module may have a molecular weight cut-off of 1×10^6 Da, 1×10^5 Da, 1×10^4 Da, 1×10^3 Da or 1×10^2 Da. The membrane module may be of an average pore size of 0.001 μm , 0.002 μm , 0.003 μm , 0.004 μm , 0.005 μm , 0.006 μm , 0.007 μm , 0.008 μm , 0.009 μm , 0.01 μm , 0.02 μm , 25 0.03 μm , 0.04 μm , 0.05 μm , 0.06 μm , 0.07 μm , 0.08 μm , 0.09 μm or 0.1 μm .

The membrane module may be operated at a transmembrane gauge pressure of about 1 bar to about 10 bars.

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The means of measuring the quantity of VOCs may be in the form of a total organic carbon analyzer. The total organic carbon analyzer may also include a suitable chamber for the measurement of inorganic carbon content.

The means of analyzing the VOCs may be in the form of an NDIR detector, a dry electrolytic conductivity detector, a thermionic ionization detector, a flame ionization detector, a thermally conductivity detector or an
5 electron capture detector.

The system may further comprise a means to transmit data comprising the total amount of VOCs present and targeted organic compounds identified to one or more offsite
10 monitoring stations.

The wireless and continuous transmission of the information may provide one with the ability to remotely monitor the total content and identify targeted VOCs in
15 samples.

Brief Description Of Drawings

The accompanying drawings illustrate a disclosed embodiment and serve to explain the principles of the
20 disclosed embodiments. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

25 Fig. 1 is a process flow diagram of the system consisting of gas stripping and membrane processes for the online monitoring and measurement of VOCs.

Fig. 2 is a process flow diagram of the system consisting
30 of a membrane process for the online monitoring and measurement of VOCs.

Fig. 3 is a graph showing a comparison of the average rejection of various compounds introduced into the disclosed system when a flat sheet membrane is used.

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Detailed Description of Drawings

Fig. 1 is a process flow diagram of the system consisting of gas stripping and membrane processes for the online monitoring and measurement of VOCs. A sample **1** is first introduced **101** via a pump **2a** and sent to a hydrocyclone **3** for the removal **102** of suspended solids **4**.

The substantially solid-free sample **1b** is then directed to a gas-stripping chamber **5** by another pump **2b**. A suitable gas **6** is used to strip any highly purgeable VOCs **7** that are present in the solid-free sample **1b**. An air compressor **8** may be used if the gas **6** is air. A mass flow controller **9** is used to control the flowrate of the gas **6** to ensure controlled gas-stripping **103**. The highly purgeable VOCs **7** that are removed from the solid-free sample **1b** through the gas-stripping **103** step are directed to an online analyzer **11** for analysis.

The purged sample **12** is then directed by a high pressure gear pump **13** into a membrane filtration skit **14**. The membrane filtration skit **14** may contain membrane modules **15** of different molecular weight cut-off (MWCO) arranged in series or in parallel. The MWCO values are in the ultrafiltration or nanofiltration range. The material of the membrane, MWCO value and configuration of the membrane modules **15** is such that the effect of the membranes modules **15** acting as a filtration system will allow the VOCs which remained unsparged in the solid-free

sample **1b** to pass through while filtering **105** the larger organic compounds that are not in the VOC range (and hence not the desired components of measurement).

5 The reject stream **12b** is drained out while the permeate stream **12a** is sent to the online analyzer **11** for analysis. The online analyzer **11** consists of an oxidation chamber **16** and a suitable detector **17**. The oxidation chamber **16** oxidizes all of the organic carbon present to
10 carbon dioxide gas. The amount of carbon dioxide gas is then measured in the detector **17**. The oxidation chamber **16** is selected so that it is suitable for the oxidation of organic carbon compound contained in both the aqueous and gaseous phases. The entry of the purged VOCs **7** or the
15 permeate stream **12a** to the analyzer **11** is controlled by a series of four-way valves **18**. The four-way valves **18** are programmed to switch at the appropriate time interval to allow an interchange between purged VOCs **7** and the permeate stream **12a**. In addition, respective calibration
20 standards (**19a**, **19b**) in both the gas and aqueous phases are also introduced into the analyzer **11** at the four-way valves **18** so that quantification of the content of VOCs may be subsequently achieved. The four-way valves **18** and analyzer **11** are periodically rinsed with deionized water
25 **24** via a pump **2c**.

The raw measurement data which is obtained is then transmitted to a computer system **21** through a datalogger
20 where it is processed to provide quantified data which indicates the total content of VOC in the sample **1**. The data can be further transmitted wirelessly through a
30 modem **22** to an offsite monitoring station **23**.

Fig. 2 is a process flow diagram of the system consisting of a membrane process for the online monitoring and measurement of VOCs. Here, like reference numerals are used to depict like elements as those in Fig. 1, but with an additional prime (') symbol. A sample **1'** is first introduced **101'** via a pump **2a'** and sent to a hydrocyclone **3'** for the removal **102'** of suspended solids **4'**.

The substantially solid-free sample **1b'** is then directed to a membrane filtration skit **14'** using a pump **13'**. The membrane filtration skit **14'** may contain membrane modules **15'** of different molecular weight cut-off (MWCO) arranged in series or in parallel. The MWCO values are in the ultrafiltration or nanofiltration range. The material of the membrane, MWCO value and configuration of the membrane modules **15'** is such that the effect of the membranes modules **15'** acting as a filtration system will allow the VOCs in the solid-free sample **1b'** to pass through while filtering **105'** the larger organic compounds that are not in the VOC range (and hence not the desired components of measurement).

The reject stream **12b'** is drained out while the permeate stream **12a'** is sent to the online analyzer **11'** for analysis. The online analyzer **11'** consists of an oxidation chamber **16'** and a suitable detector **17'**. The oxidation chamber **16'** oxidizes all organic carbon present to carbon dioxide gas. The amount of carbon dioxide gas is then measured in the detector **17'**. The oxidation chamber **16'** is selected so that it is suitable for the oxidation of organic carbon compound contained in both the aqueous and gaseous phases. The entry of the permeate stream **12a'** to the analyzer **11'** is controlled by a four-

way valve 18'. In addition, a calibration standard (19b')
in the aqueous phase is also introduced into the analyzer
11' at the four-way valve 18' so that quantification of
the content of VOCs may be subsequently achieved. The
5 four-way valve 18' and analyzer 11' are periodically
rinsed with deionized water 24' via a pump 2c'.

The raw measurement data which is obtained is then
transmitted to a computer system 21' through a datalogger
10 20' where it is processed to provide quantified data
which indicates the total content of VOC in the sample
1'. The data can be further transmitted wirelessly
through a modem 22' to an offsite monitoring station 23'.

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Examples

Non-limiting examples of the invention will be further
described in greater detail by reference to specific
Examples, which should not be construed as in any way
20 limiting the scope of the invention.

Example 1: Rejection of various compounds introduced into
the disclosed system using gas-stripping and a flat sheet
membrane

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Tests were conducted based on the process shown in Fig.
1. In the tests, samples each containing 200ppm of the
VOCs (made up with deionized water) and non-VOCs listed
in Table 1 were analysed.

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Table 1

No.	Compounds	Molecular Wt.	Boiling Pt. (°C)
1	Ethanol	46.1	78
2	Acetone	58.1	56
3	Acetic acid	60.1	118
4	Isopropyl alcohol (IPA)	60.1	82
5	Dichloromethane	84.9	40
6	Hexane	86.2	69
7	Ethyl acetate	88.1	77
8	Toluene	92.1	111
9	Butyl Acetate	116.2	126
10	Sodium dodecyl sulphate (SDS)	288.4	N/A
11	Polysorbate 80 (PS80)	1310	N/A

No pre-treatment of the samples was carried out. Air from a purified air cylinder was used in the gas stripping process. Approximately 200 mL of a sample was sparged with the inert gas for 2 minutes at a flow rate of 5 L/min. The gas sparging was conducted at room temperature and 1 bar gauge pressure. A semi-permeable polyethersulfone flat sheet membrane (Koch HFK-328) was used in the membrane filtration process, with the filtration pressure adjusted to 6 bars. The filtration process was carried out at room temperature.

The results of the tests conducted are provided in Table 2, and show that gas stripping is effective for the stripping of small chain organic compounds that are non-polar, such as dichloromethane, hexane and toluene. The measurement of these VOCs that have low miscibility with water are usually relatively straightforward as they can be easily stripped into the gaseous phase and measured thereafter. However, compounds that are polar and miscible with water such as ethanol, acetone, acetic acid and isopropyl alcohol mostly still remained in the

aqueous phase after the stripping process. Consequently, if the method to measure VOCs in the aqueous phase is based solely on gas stripping, then only a small amount of these polar VOCs that are present can be measured.

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Certain partially miscible, short chain organic compounds such as ethyl acetate and butyl acetate are partially stripped into the gas phase according to their affinity to water; hence they are only detected partially by the gas stripping method. Large organic compounds such as sodium dodecyl sulphate and polysorbate 80 remain unstripped and remain in the aqueous phase after gas sparging.

15 After gas stripping, the liquid samples together with any remaining organic compounds were then channelled to the filtration section. In this section, the short chain organic compounds passed through to the permeate side while larger organic compounds (non-VOCs) such as SDS and PS80 were filtered away into the retentate so they did not add to the results significantly.

The VOCs in the permeate were then measured. A catalytic combustion chamber was used to oxidise the VOCs resulting from both gas stripping and filtration processes into CO₂. The oxidised VOCs were subsequently measured by an NDIR detector.

30 The amounts of VOC that were measured from the gas stripping and filtration sections were then combined to give an overall measured value of the concentration of VOCs. It can be seen from Table 2 that at least 90% detection were achieved for all types of VOCs regardless of their polarity and affinity to water.

Table 2

No	Compound	Initial (as TOC, ppm)	After Gas Stripping		After Membrane Filtration		Total Measured (%)
			Measured (as TOC, ppm)	Percentage measured (%)	Measured (as TOC, ppm)	Percentage measured (%)	
1	Ethanol	87.1	2.3	2.7	79.7	91.5	94.2
2	Acetone	92.1	8.5	9.2	81.8	88.9	98.1
3	Acetic acid	87.8	0.6	0.7	83.7	95.3	96.0
4	Isopropyl alcohol (IPA)	106.2	0.5	0.5	102.9	96.9	97.4
5	Dichloromethane	23.7	23.6	99.8	0.0	0.0	99.8
6	Hexane	0.81	0.76	94.3	0.0	0.0	94.3
7	Ethyl acetate	96.3	36.9	38.3	55.4	57.6	95.9
8	Toluene	91.1	88.8	97.5	0.0	0.0	97.5
9	Butyl Acetate	107.6	90.4	84.1	15.4	14.3	98.4
10	Sodium dodecyl sulphate (SDS)	89.2	0.5	0.6	7.94	8.9	8.9
11	Polysorbate 80 (PS80)	132.2	0.3	0.3	3.2	2.5	2.5

Example 2: Rejection of various compounds introduced into the disclosed system using a flat sheet membrane

Tests were conducted based on the process shown in Fig.

- 5 2. This arrangement used the filtration approach directly. Such an arrangement is suitable when the VOCs of interest to be detected are semi-miscible or miscible compounds in aqueous phase. Samples each containing 200ppm of the VOCs (made up with deionized water) and
10 non-VOCs listed in Table 3 were analysed.

Table 3

No.	Compounds	Molecular Wt.	Boiling Pt. (°C)
1	Ethanol	46.1	78
2	Acetone	58.1	56
3	Acetic acid	60.1	118
4	Isopropyl alcohol (IPA)	60.1	82
5	Ethyl acetate	88.1	77
6	Butyl Acetate	116.2	126
7	Sodium dodecyl sulphate (SDS)	288.4	N/A
8	Polysorbate 80 (PS80)	1310	N/A

- No pre-treatment of the samples was carried out. A semi-
15 permeable polyethersulfone flat sheet membrane (Koch HFK-328) was used in the tests, with the filtration pressure adjusted to 6 bars. All tests were conducted at room temperature.

- 20 The membrane type, configuration and operating parameters were optimised to allow VOCs in the aqueous phase to pass through in the permeate while rejecting all the other longer chain organic compounds. It can be seen from Fig. 3 and Table 4 that the long chain organic compounds (SDS

and PS80) were mainly rejected while the VOCs were permitted to pass through in the permeate for measurement. A catalytic combustion chamber was used to oxidise the VOCs into CO₂ which were then analysed by an NDIR detector. The TOC values and percentage detected for each of the samples are shown in Table 4.

Table 4

No.	Compound	Concentration (TOC, ppm)		Detection (%)
		Sample	Measured	
1	Ethanol	77.6	75.1	96.7
2	Acetone	88.5	86.8	98.1
3	Acetic acid	84.9	81.4	95.9
4	Isopropyl alcohol (IPA)	89.3	87.4	97.9
5	Ethyl acetate	88.8	85.3	96.0
6	Butyl Acetate	91.3	80.3	88.0
7	Sodium dodecyl sulphate (SDS)	112.3	8.0	7.1
8	Polysorbate 80 (PS80)	139.1	4.0	2.9

It is observed that the ability of the system to detect the VOCs was more than 95% in the case of using ethanol, acetone, acetic acid, isopropyl alcohol and ethyl acetate. SDS and PS80 (i.e., non-VOCs) made up of longer chain organic compounds were generally filtered off by the membrane in use.

Applications

The continuous and reliable online detection of VOCs is an important feature in the provision of potable water (e.g. in aquifers and treated water) and in sewerage
5 networks.

In many countries that rely on groundwater sources for drinking water, the identification of source-control strategies or enhancing existing measures may be
10 warranted if anthropogenic VOC compounds are detected frequently in groundwater. The reliable detection of a VOC in groundwater will also be of concern because it can additionally be indicative that a pathway exists by which other persistent and potentially toxic compounds other
15 than VOCs may reach the supply wells of drinking water.

Made up of low molecular weight organic compounds, VOCs can permeate even final-stage reverse osmosis (RO) membranes commonly found in the production of ultrapure
20 water based on water reclamation processes. The production of ultrapure water therefore requires stringent monitoring of any VOCs occurring in the overall process of water treatment. Accordingly operators of water treatment plants rely on VOC detection systems to
25 provide them with the ability to monitor the quality of the water produced. The continuous monitoring of the presence of VOCs is important starting from prevailing upstream processes (i.e., in the influent waste water stream) of such water treatment works. The early
30 detection of VOCs at the source of a water reclamation plant provides plant operators with ample time to react with the necessary measures and prevent any sudden shutdown of the plants.

The current disclosure also provides for the reliable and continuous monitoring at localized sites where trade effluent may be discharged. This will be applicable in an industrial setting where any treated effluent may be
5 discharged into a sewerage network or allowed to be discharged into a natural occurring body of water.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the
10 person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A method of quantifying the total amount of VOCs in a sample comprising the steps of:

- (a) providing a feed stream of polar and non-polar VOCs in a liquid phase;
- (b) separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;
- (c) passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and
- (d) measuring the quantity of VOCs in the volatile phase of step (b) and the permeate stream of step (c) to calculate the total amount of VOCs in said sample.

2. A method of identifying targeted VOCs present in a sample, comprising the steps of:

- (a) providing a feed stream of polar and non-polar VOCs in a liquid phase;
- (b) separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;
- (c) passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC permeate stream and non-VOC retentate stream; and
- (d) analyzing the VOCs in the volatile phase of step (b) and the permeate stream of step (c) to thereby identify said targeted VOCs in said sample.

3. The method according to claim 1 or claim 2, wherein said separating step comprises gas stripping said sample with a suitable gas.

5 4. The method according to claim 1 or claim 2, wherein said permeable barrier is a membrane module.

5. The method according to claim 2, wherein said analyzing step comprises the step of subjecting the
10 targeted VOCs to at least one detector.

6. The method according to claim 3, wherein said gas is selected from the group consisting of N₂, H₂, Ar, O₂, Kr, Xe, and ambient air.

15

7. The method according to claim 4, wherein said membrane module comprises a polymeric material.

8. The method according to claim 7, wherein said
20 polymeric material is selected from one of the following: cellulose acetate (CA), nitrocellulose (CN), cellulose esters (CE), polysulfone (PS), polyether sulfone (PES), polyacrylonitrile (PAN), polyamide, polyimide, polyethylene (PE), polypropylene (PP),
25 polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF) and polyvinylchloride (PVC).

9. The method according to claim 4, wherein said membrane module comprises a ceramic material.

30

10. The method according to claim 9, wherein said ceramic material comprises at least one of the following: alumina, zirconia, titania or silicon carbide.
- 5 11. The method according to claim 4 or any of claims 7 to 10, wherein said membrane module has a molecular weight cut-off of at most about 1×10^6 Da.
- 10 12. The method according to claim 4 or any of claims 7 to 11, wherein said membrane module is of an average pore size selected from between about 0.001 μm to about 0.1 μm .
- 15 13. The method according to claim 4 or any of claims 7 to 12, wherein said membrane module is in a spatial configuration selected from the group consisting of flat sheets, hollow fibers, tubes and spiral wound structures.
- 20 14. The method according to claim 4 or any of claims 7 to 13, wherein said membrane module comprises of membranes arranged either in parallel or in series.
- 25 15. The method according to claim 4 or any of claims 7-14, wherein said membrane module is operated at a transmembrane gauge pressure of about 1 bar to about 10 bars.
- 30 16. The method according to any one of the preceding claims, wherein said VOCs are organic halides selected from the group consisting of dichloroacetonitrile, chloroform, iodobenzene, 1,1,2-trichlorotrifluoroethane,

trichloroethylene, perchloroethylene, carbon
tetrachloride, chloroform, 1,1-dichloroethene, vinyl
chloride, trans-1,2-dichloroethene, cis-1,2-
dichloroethene, dichloromethane, 1,1,1-trichloroethane,
5 1,1,2-trichloroethane, 1,2-dichloroethane, bromoform,
bromodichloromethane and chlorodibromomethane, ethanol,
acetone, acetic acid, isopropyl alcohol (IPA),
dichloromethane, hexane, ethyl acetate, toluene, butyl
acetate, benzene, 1,2,4-trichlorobenzene, 1,4-
10 dichlorobenzene, 1,2-dichlorobenzene, xylene,
chlorobenzene, ethylbenzene and 2-propenamide.

17. The method according to any one of the preceding
claims, further comprising the step of (e) pre-treating
15 said sample to remove solids therefrom.

18. The method according to claim 17, wherein the step of
pre-treating comprises one or more of the steps from the
group consisting of filtrating, centrifuging,
20 sedimenting, coagulating and flocculating.

19. A system to quantify the total amount of VOCs in a
sample comprising the following:

(a) means of providing a feed stream of polar and non-
25 polar VOCs in a liquid phase;

(b) means of separating the feed stream into a volatile
phase that predominantly contains non-polar VOCs and a
liquid phase that predominantly contains polar VOCs;

(c) means of passing the liquid phase through a permeable
30 barrier to separate the polar VOCs into a polar VOC
permeate stream and non-VOC retentate stream; and

(d) means of measuring the quantity of VOCs in the volatile phase of step (b) and the permeate stream of step (c) to calculate the total amount of VOCs in said sample.

5

20. A system to identify targeted VOCs comprising the following:

(a) means of providing a feed stream of polar and non-polar VOCs in a liquid phase;

10 (b) means of separating the feed stream into a volatile phase that predominantly contains non-polar VOCs and a liquid phase that predominantly contains polar VOCs;

(c) means of passing the liquid phase through a permeable barrier to separate the polar VOCs into a polar VOC
15 permeate stream and non-VOC retentate stream; and

(d) means of analyzing the VOCs in the volatile phase of step (b) and the permeate stream of step (c) to thereby identify said targeted VOCs in said sample.

20 21. The system according to claim 19 or 20, wherein said means of separating the feed stream is a gas stripper.

22. The system according to claim 19 or 20, wherein said permeable barrier is a membrane module.

25

23. The system according to claim 19, wherein said means of measuring the quantity of VOCs is a total organic carbon analyzer.

24. The system according to claim 20, wherein said means of analyzing the VOCs is a mass spectrometer.

25. The system according to claim 19, further comprising
5 (e) a means of transmitting data comprising the total amount of VOCs present to one or more offsite monitoring stations.

26. The system according to claim 20, further comprising
10 (e) a means of transmitting data comprising identified targeted VOCs to one or more offsite monitoring stations.