

An *in situ* real time monitoring system for trace analytes in water

BACKGROUND

5 The detection of trace concentrations of metals and other contaminants in water can be difficult to accomplish with a degree of certainty. The original technique used for analysis of trace analytes in water was a "grab sample" analysis, whereby a sample was collected in an open container at a single point in time at, or near, the surface of the water body to be analysed. As such, a grab sample only reflects the conditions at the point in time that the
10 sample was collected, and then only if the sample was properly collected. Problems with grab sampling include changes or loss of analytes during sampling, transport, handling and storage of samples.

The technique of diffusive gradients in thin-films (DGT) has been developed as an
15 alternative method. Analytes that have been measured by the DGT technique include Ni, Cu, Fe, Mn, Zn, Cd, Mg, Ca and phosphorus.

The technique of diffusive gradients in thin films (DGT) has been used for trace analysis in the environment in which labile analytes freely diffuses through a thin hydrogel layer (e.g. an
20 acrylamide based gel, crossed linked with an agarose-derived cross linker), which acts as a well-defined diffusion layer, and are then accumulated on an underlying phase containing a fixed binding agent (e.g. ion-exchangeable Chelex-100 resin or ferrihydrite). DGT relies on the establishment of a steady state concentration gradient in the diffusion layer so that Fick's First Law can be used to calculate unknown concentrations. By measuring the amount (*M*)
25 of analyte on the binding agent, a time-averaged concentration (*C*) over the deployment time (*t*) is estimated, as the thickness (*Δg*) and the surface area (*A*) of exposure are known (Eq. 1) (Davison, W.; Fones, G.; Harper, M.; Teasdale, P.; Zhang, H., Dialysis, DET and DGT: In situ diffusional techniques for studying water, sediments and soils. In *In Situ Monitoring of Aquatic Systems*, John Wiley & Sons Ltd.: 2000; Vol. 6, pp 495-569):

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$$C = \frac{M\Delta g}{DA t} \quad (1)$$

Although the DGT technique has overcome the constraints of the traditional "grab sampling" methods, which have the issues discussed above, with its *in situ* preconcentration feature,
35 this technique still requires elution of the analyte from the binding agent in order to perform the calculation required in equation 1 (Li, W.; Teasdale, P. R.; Zhang, S.; John, R.; Zhao, H.,

Application of a poly(4-styrenesulfonate) liquid binding layer for measurement of Cu^{2+} and Cd^{2+} with the diffusive gradients in thin-films technique. Analytical Chemistry 2003, 75, (11), 2578-2583). This means that there is a delay in obtaining the results and requires extra steps in sample preparation, which can adversely affect the accuracy of the resulting analysis. This is a fact acknowledged by the authors of this technique, who made use of a correction factor for the mass obtained, as it is frequently impossible to extract all of the desired analyte from the binding agent layer.

Therefore, there remains a need for improved methods of sampling various waters.

SUMMARY OF INVENTION

In a first aspect of the invention, there is provided a preconcentration device for measuring the amount of a trace analyte in a water body, the device comprising a vessel having an opening, a hydrated polymer membrane that covers the opening in the vessel, and an aqueous solution of a polyelectrolyte polymer provided in the vessel and in direct contact with the membrane.

In certain embodiments of the invention, the polyelectrolyte polymer may be a polycationic polymer (e.g. the polycationic polymer may be selected from the group consisting of one or more of poly(4-styrenesulfonate) and, more preferably, polydiallyldimethylammonium chloride).

In further embodiments, the polyelectrolyte polymer may have a weight average molecular weight of from 60,000 Daltons to 350,000 Daltons (e.g. from 200,000 Daltons to 350,000 Daltons).

In yet further embodiments, the polymer of the hydrated polymer membrane:

(a) may have a weight average molecular weight cut-off of 12,000 Daltons;

and/or

(b) may be a hydrated cellulose polymer membrane.

In yet still further embodiments, the preconcentration device may further comprise a light absorbance detection unit, where the vessel is adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit (e.g. the vessel and light absorbance detection unit are brought into fluid communication with each other by a fluid communication means or apparatus). For example, the light absorbance detection unit may

comprise a detection chamber for containing the sample, a light emitting LED and a photodiode (e.g. a LED) attached to a measuring unit (e.g. a multimeter), wherein the light emitting LED and the photodiode are arranged such that the light from the light emitting LED passes through the detection chamber before contacting the photodiode.

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In certain embodiments, the detection chamber may further comprise at least one inlet and an outlet, where the at least one inlet is adapted to admit the sample of the aqueous solution of a polyelectrolyte and/or a detection reagent.

10 In certain embodiments, the analyte may be selected from one or more of the group selected from a phosphate, arsenic and an arsenate.

In a second aspect of the invention, there is disclosed a use of an aqueous solution of a polyelectrolyte polymer to trap a trace analyte present in a water body for subsequent
15 analysis.

In certain embodiments of the second aspect of the invention, the polyelectrolyte polymer may be a polycationic polymer (e.g. the polycationic polymer may be selected from the group consisting of one or more of poly(4-styrenesulfonate) and, more preferably,
20 polydiallyldimethylammonium chloride). In further embodiments, the polyelectrolyte polymer may have a weight average molecular weight of from 60,000 Daltons to 350,000 Daltons (e.g. from 200,000 Daltons to 350,000 Daltons).

In a third aspect of the invention, there is disclosed a method of analysing the amount of a
25 trace analyte in a water body, wherein the method comprises the steps of:

(a) submerging a preconcentration device in a water body, the preconcentration device comprising:

a vessel having an opening;

a hydrated polymer membrane that covers the opening in the vessel;

30 and

an aqueous solution of a polyelectrolyte polymer provided in the vessel and in direct contact with the membrane;

(b) removing an aliquot of the aqueous solution of a polyelectrolyte polymer after a period of time has passed, and providing the same to a light absorbance
35 detection unit comprising a detection chamber, a light emitting LED and a photodiode attached to a measuring unit, optionally the aliquot is obtained by removing the preconcentration device from the water body;

- (c) adding a chemical reagent that reacts with the analyte to produce a colour before or after providing the aliquot of the aqueous solution to the detection chamber;
- (d) measuring the light absorbance following reaction of the chemical reagent and analyte and calculating the concentration of the analyte in the water body.

Certain embodiments of this aspect may be derived from the first aspect of the invention.

In further embodiments, the preconcentration device may be adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit (e.g. the vessel and light absorbance detection unit are brought into fluid communication with each other by a fluid communication means or apparatus).

In a third aspect of the invention, there is disclosed an apparatus for analyte detection and/or measurement of a water body, comprising a floatable and/or a submersible vessel; and the preconcentration device of the first aspect of the invention (and embodiments thereof), wherein the preconcentration device is adapted to enable at least the membrane of the preconcentration device to be in direct contact with water from the water body.

Further aspects and embodiments of the invention are provided in the following numbered clauses.

1. A preconcentration device for measuring the amount of a trace analyte in a water body, the device comprising:

- a vessel having an opening;
- a hydrated polymer membrane that covers the opening in the vessel; and
- an aqueous solution of a polyelectrolyte polymer provided in the vessel and in direct contact with the membrane.

2. The preconcentration device of Clause 1, wherein the polyelectrolyte polymer is a polycationic polymer.

3. The preconcentration device of Clause 2, wherein the polycationic polymer is selected from the group consisting of one or more of polydiallyldimethylammonium chloride and poly(4-styrenesulfonate).

4. The preconcentration device of Clause 3, wherein the polycationic polymer is polydiallyldimethylammonium chloride.

5. The preconcentration device of any one of the preceding Clauses, wherein the polyelectrolyte polymer has a weight average molecular weight of from 60,000 Daltons to 350,000 Daltons.

6. The preconcentration device of Clause 5, wherein the polyelectrolyte polymer has a weight average molecular weight of from 200,000 Daltons to 350,000 Daltons.

7. The preconcentration device of any one of the preceding Clauses, wherein the polymer of the hydrated polymer membrane:

- (a) has a weight average molecular weight cut-off of 12,000 Daltons; and/or
- (b) is a hydrated cellulose polymer membrane.

8. The preconcentration device of any one of the preceding Clauses, wherein the preconcentration device further comprises a light absorbance detection unit, where the vessel is adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit (e.g. the vessel and light absorbance detection unit are brought into fluid communication with each other by a fluid communication means or apparatus).

9. The preconcentration device of Clause 8, wherein the light absorbance detection unit comprises a detection chamber for containing the sample, a light emitting LED and a photodiode attached to a measuring unit, wherein the light emitting LED and the photodiode are arranged such that the light from the light emitting LED passes through the detection chamber before contacting the photodiode.

10. The preconcentration device of Clause 9, wherein the photodiode is a LED and/or the measuring unit is a multimeter.

11. The preconcentration device of any one of Clauses 9 or 10, wherein the detection chamber further comprises at least one inlet and an outlet, where the at least one inlet is adapted to admit the sample of the aqueous solution of a polyelectrolyte and/or a detection reagent.

12. The preconcentration device of any one of the preceding Clauses, wherein the analyte is selected from one or more of the group selected from a phosphate, arsenic and an arsenate.

13. A use of an aqueous solution of a polyelectrolyte polymer to trap a trace analyte present in a water body for subsequent analysis.

14. The use of Clause 13, wherein the polyelectrolyte is a polycationic polymer.

15. The use of Clause 14, wherein the polycationic polymer is selected from the group consisting of one or more of polydiallyldimethylammonium chloride and poly(4-styrenesulfonate).

16. The use of Clause 15, wherein the polycationic polymer is polydiallyldimethylammonium chloride.

17. The use of any one of Clauses 13 to 16, wherein the polyelectrolyte polymer has a weight average molecular weight of from 60,000 Daltons to 350,000 Daltons.

18. The use of Clause 17, wherein the polyelectrolyte polymer has a weight average molecular weight of from 200,000 Daltons to 350,000 Daltons.

19. A method of analysing the amount of a trace analyte in a water body, wherein the method comprises the steps of:

(a) submerging a preconcentration device in a water body, the preconcentration device comprising:

a vessel having an opening;

a hydrated polymer membrane that covers the opening in the vessel;

and

an aqueous solution of a polyelectrolyte polymer provided in the vessel and in direct contact with the membrane;

(b) removing an aliquot of the aqueous solution of a polyelectrolyte polymer after a period of time has passed, and providing the same to a light absorbance detection unit comprising a detection chamber, a light emitting LED and a photodiode attached to a measuring unit, optionally the aliquot is obtained by removing the preconcentration device from the water body;

- (c) adding a chemical reagent that reacts with the analyte to produce a colour before or after providing the aliquot of the aqueous solution to the detection chamber;
- (d) measuring the light absorbance following reaction of the chemical reagent and analyte and calculating the concentration of the analyte in the water body.

20. The method of Clause 19, wherein the polyelectrolyte polymer is a polycationic polymer.

21. The method of Clause 20, wherein the polycationic polymer is selected from the group consisting of one or more of polydiallyldimethylammonium chloride and poly(4-styrenesulfonate).

22. The method of Clause 21, wherein the polycationic polymer is polydiallyldimethylammonium chloride.

23. The method of any one of Clauses 19 to 22, wherein the polyelectrolyte polymer has a weight average molecular weight of from 60,000 Daltons to 350,000 Daltons.

24. The method of Clause 23, wherein the polyelectrolyte polymer has a weight average molecular weight of from 200,000 Daltons to 350,000 Daltons.

25. The method of any one of Clauses 19 to 24, wherein the polymer of the hydrated polymer membrane:

- (a) has a weight average molecular weight cut-off of 12,000 Daltons; and/or
- (b) is a hydrated cellulose polymer membrane.

26. The method of any one of the Clauses 19 to 25, wherein the preconcentration device is adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit (e.g. the vessel and light absorbance detection unit are brought into fluid communication with each other by a fluid communication means or apparatus).

27. The method of any one of Clauses 19 to 26, wherein the photodiode is a LED and/or the measuring unit is a multimeter.

28. The method of any one of Claims 19 to 27, wherein the detection chamber further comprises at least one inlet and an outlet, where the at least one inlet is adapted to admit the sample of the aqueous solution of a polyelectrolyte and/or a detection reagent.

29. The method of any one of Claims 19 to 28, wherein the analyte is selected from one or more of the group selected from a phosphate, arsenic and an arsenate.

30. An apparatus for analyte detection and/or measurement of a water body, comprising: a floatable and/or a submersible vessel; and

the preconcentration device of any one of Claims 1 to 12, wherein the preconcentration device is adapted to enable at least the membrane of the preconcentration device to be in direct contact with water from the water body.

FIGURES

The invention will now be described in further detail below, with the aid of the following figures.

Fig. 1 depicts a preconcentration device for measuring the amount of a trace analyte in a water body.

Fig. 2 depicts the same device in combination with a detection system.

DESCRIPTION

An *in situ* real time monitoring system is invented for monitoring of trace concentrations of analytes in water to replace the problematic, time consuming and costly grab sampling and lab based methods. The system is based on the *in situ* quantitative sampling technique of diffusive gradients in thin films (DGT) by employing an aqueous solution containing a high affinity polymer as a binding phase instead of the use of a traditional hydrogel to form complexes with an analyte (e.g. phosphates). A diffusive membrane with smaller molecular weight cut off than the polymer molecular weight is used to keep the complexed analyte in the solution while allowing trace concentrations of analytes to freely diffuse through the membrane. The amount of complexed analyte in the polymer solution is then determined by measuring its light absorbance using a pair of light emitting diodes (LED) before the concentration of analyte in water is calculated with the DGT equation. The use of an aqueous solution binding phase allows easy sampling and direct measurements of the light

absorbance using small and low cost LED bulbs. The combination of DGT and LED provides a real time *in situ* monitoring system for accurate measurements of trace analyte concentrations.

- 5 With reference to Fig. 1, there is provided a preconcentration device (100) for measuring the amount of a trace analyte in a water body, the device comprising a vessel (110; e.g. a polypropylene tube open at one end only) having an opening (120) a hydrated polymer membrane (130) that covers the opening in the vessel (110) and an aqueous solution of a polyelectrolyte polymer (140) provided in the vessel (110) and in direct contact with the
- 10 membrane (130). As shown in Fig. 1 the device may also contain a gasket (150; e.g. a rubber gasket) and a clamp (160), which are used in combination to hold the membrane (130; e.g. a perspex clamp) over the opening (120).

As shown in Fig. 1, an analyte (200) diffuses through the hydrated polymer membrane (130)

15 and comes into contact with the aqueous solution of a polyelectrolyte polymer (140), which binds to the analyte. Particular analytes that may be mentioned include a phosphate, arsenic and an arsenate.

When used herein, the polyelectrolyte polymers that may be mentioned herein include

20 polycationic and polyanionic polymers. Polycationic polymers that may be mentioned herein include poly(4-styrenesulfonate) and polydiallyldimethylammonium chloride. A particular polyanionic polymers that may be mentioned herein is polydiallyldimethylammonium chloride.

The molecular weight of the polyelectrolyte polymers mentioned herein may have a weight

25 average molecular weight of from 60,000 Daltons to 350,000 Daltons. Particular polyelectrolyte polymers mentioned herein may have a weight average molecular weight of from 200,000 Daltons to 350,000 Daltons.

As mentioned hereinbefore, the hydrated polymer membrane (130) enables an analyte from

30 a body of water to come into contact with the aqueous solution of a polyelectrolyte polymer (140) by diffusion through said membrane. In particular embodiments, the polymer of the hydrated polymer membrane has a weight average molecular weight cut-off of 12,000 Daltons and/or is a hydrated cellulose polymer.

35 As shown in Fig. 2, the preconcentration device may also further comprises a light absorbance detection unit (300), where the vessel (110) is adapted to enable a sample of the aqueous solution of a polyelectrolyte (140) to be provided to the detection unit (e.g. the

vessel and light absorbance detection unit are brought into fluid communication with each other by a fluid communication means or apparatus). It will be appreciated that the vessel (110) may be permanently attached to the detection unit, or may be adapted to be detachable from and re-attachable to the detection unit (300), depending on the intended use. For example, the vessel portion of the preconcentration device (i.e. 110-160), may be deployed separately into a body of water, then recovered after a period of time has passed and attached to the detection unit (300) to provide a sample of the aqueous solution of a polyelectrolyte (140) for measurement by the detection unit (300). Alternatively, the vessel and the detection unit portions of the preconcentration device may be integrated into a floatable and/or submersible vessel that may be autonomous and fitted with automated detection equipment, allowing for samples to be taken periodically and fed back to a remote control centre. For example, there is also disclosed an apparatus for analyte detection and/or measurement of a water body, comprising a floatable and/or a submersible vessel; and the preconcentration device as described herein, wherein the preconcentration device is adapted to enable at least the membrane of the preconcentration device to be in direct contact with water from the water body.

As shown in Fig. 2, the light absorbance detection unit (300) comprises a detection chamber (310) for containing the sample, a light emitting LED (320) and a photodiode (330) attached to a measuring unit (340), wherein the light emitting LED (320) and the photodiode (330) are arranged such that the light from the light emitting LED passes through the detection chamber (310) before contacting the photodiode (330).

As shown in Fig. 2, the photodiode (330) may also be an LED that is attached to a multimeter (i.e. the measuring unit (340)). It will be appreciated that any suitable measuring unit may be attached to the LED/photodiode.

Fig. 2 also shows that the vessel (110) is in fluid communication with the detection chamber (310) by way of a tube or pipe (171) that is in contact with the aqueous solution of a polyelectrolyte (140) and passes through an outlet (170) on the vessel (110) to an inlet (350) on the detection chamber (310). In order to obtain an absorbance reading a colour reagent that causes a colour change in the presence of the desired analyte must also be added to the detection chamber, this may be accomplished by providing a vessel containing a colour reagent and a pipe or tube (361) attached to a further inlet (370) on the detection chamber. It will be appreciated that the device can be configured to ensure that an appropriate amount of the aqueous solution of a polyelectrolyte (140) and the colour reagent are provided to the detection chamber for measurement. It will also be appreciated that there need only be a

single inlet to the detection chamber. The detection chamber may also be fitted with an outlet (380) by way of a tube or pipe (381) to a waste container.

In operation, and with reference to Figs. 1 and 2, the device operates through a method of analysing the amount of a trace analyte in a water body, wherein the method comprises the steps of:

- (a) submerging a preconcentration device (100) in a water body, the preconcentration device comprising:

a vessel (110) having an opening (120);

a hydrated polymer membrane (130) that covers the opening (120) in the vessel (110); and

an aqueous solution of a polyelectrolyte polymer (140) provided in the vessel and in direct contact with the membrane;

- (b) removing an aliquot of the aqueous solution of a polyelectrolyte polymer (140) after a period of time has passed, and providing the same to a light absorbance detection unit (300) comprising a detection chamber (310), a light emitting LED (320) and a photodiode (330) attached to a measuring unit (340), optionally the aliquot is obtained by removing the preconcentration device from the water body;

- (c) adding a chemical reagent that reacts with the analyte to produce a colour before or after providing the aliquot of the aqueous solution to the detection chamber;

- (d) measuring the light absorbance following reaction of the chemical reagent and analyte and calculating the concentration of the analyte in the water body.

The polyelectrolyte polymer and the polymer of the hydrated polymer membrane may be polymers as hereinbefore described.

As noted hereinbefore, the preconcentration device may be adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit (e.g. the vessel and light absorbance detection unit are brought into fluid communication with each other by a fluid communication means or apparatus), as shown schematically in Fig. 2.

As described above, the technique of diffusive gradients in thin films (DGT) has been used for trace analysis in the environment in which labile analytes freely diffuse through a thin hydrogel layer and are then accumulated on an underlying phase containing a fixed binding agent. This process effectively maintains a diffusive gradient within the diffusive layer that is

described by Fick's law of diffusion. By measuring the amount (M) of analyte on the binding agent, a time-averaged concentration (C) over the deployment time (t) is estimated, as the thickness (Δg) and the surface area (A) of exposure are known (Eq. 1):

$$C = \frac{M\Delta g}{DA t} \quad (1)$$

An aqueous solution containing a large affinity polymer to form complexes with analytes is used as the DGT binding phase in our invention. A diffusive membrane with known thickness (Δm), exposure area (A) and smaller molecular weight cut off than the polymer molecular weight is used to keep the complexed analytes inside the polymer solution while allowing analytes to freely diffuse through the membrane (Fig. 1). The light absorbance (a) of the polymer complexed analytes with known volume (V), is measured directly by paired light emitting diodes (LED) without elution steps (Fig. 2). This combination of the *in situ* quantitative preconcentration technique and direct absorbance measurements of LED provides a real time monitoring system for analytes. The LEDs are mounted on both top and bottom of a detection chamber with pumps to flow the complexed polymer solution and a color-generating reagent through the chamber. The concentration of analytes in water (C) can be calculated based Fick's law of diffusion (Eq. 2) when the preconcentration device is deployed in water for a time period of time (t),

$$C = \frac{a}{\epsilon b D} \frac{V \Delta m}{A t} \quad (2)$$

where ϵ , D and b are absorptivity of the complexed polymer solution, diffusion coefficient of the analytes in the membrane and the thickness of the detection chamber for light to pass through, respectively. It will be appreciated that the time mentioned herein is the length of exposure of the vessel (110) to the water of the water body. This may be any time from 20 minutes (e.g. 2 hours) to 24 hours or longer.

Equation (2) is derived by replacing M in equation (1) using the concentration of the analyte in the polymer multiplied by the volume of the analytical sample and subsequently, the concentration of the analyte in the polymer is replaced using Beer's law to solve for this concentration, as explained in more detail below.

This invention offers numerous advantages over the grab sampling and laboratory measurement methods and the traditional DGT technique.

(i) It does not require the elution steps in the traditional DGT technique and it has high sensitivity/accuracy compared with grab sample methods.

(ii) The use of an aqueous polymer solution instead of the hydrogel used in traditional DGT allows for prolonged periods of *in situ* real time monitoring by periodically replenishing the device with fresh polymer solution.

(iii) The system costs of construction and maintenance are lower compared to the traditional DGT technique and are less labour intensive compared with the grab sampling method.

(iv) It has low energy consumption (the LED bulbs and signal receiving meter).

(v) It is a self-calibrated system.

(vi) It can either be used as a portable device or at a fixed location. Alternatively, it can be fixed to an autonomous vessel (e.g. a floatable and/or submersible vessel).

(vii) It can be extended to applications for other types of analytes.

The system can be used for applications of environmental monitoring of trace contaminants in water, e.g. by water agencies, regulatory and enforcement agencies, research institutes, commercial organizations, etc.

The diffusive membrane can be replaced easily when the device is used for longer term deployment to avoid possible biofouling effects (e.g. on a quarterly basis).

The main competing ways to the application of this system may include (i) the existing traditional DGT methods which tend to be offline, (ii) direct online monitoring methods without preconcentration which are limited by their low detection sensitivity.

Other modes of the system include the use of radiation detectors to directly measure the amount of radionuclides preconcentrated in the complexed polymer solution and other detection methods for varying analyte species.

The invention will now be illustrated based upon the following examples.

EXAMPLES

General Procedure

- 5 A system according to Figure 1 was provided. In the system of Figure 1, the membrane had a thickness of 0.005 cm and a contact surface area of from 10 cm² to 2 cm² (i.e. the area of the membrane in contact with water on one face and with the aqueous polymer solution on the other face). The defined area and thickness for the membrane are to form a diffusive layer for the analyte (e.g. phosphate) to diffuse from the sample into the device.
- 10 Subsequently, the analyte reaches the compartment containing the polymer solution where the analyte becomes bound to the polymer (this is referred to as the binding layer).

The system was pre-calibrated by fixing the diffusion coefficient (D) and absorbability (ϵ). These values are constant and can be measured prior to deployment. The detection

15 chamber/cuvette, has a path length of 1 cm and a volume of 1 mL (or a volume of 5 mL and a path length of 5 mL in certain embodiments).

1. D is determined in a lab using the specific device used in subsequent measurements. So is ϵ , which can be determined in lab with the same LED detection chamber design
- 20 used in actual sample measurements. D and ϵ are constant.

To do this, a cell consisting of two compartments separated by the membrane described above is used. One compartment contains the aqueous polymer solution, and the other contains an analyte solution. Mass transfer of the analyte to the

25 polymer solution compartment over time is measured at varying time intervals. A mass versus time curve is then drawn. The slope of the curve is then used to calculate D (at 25°C) using equation (3) below.

$$D = \frac{\text{slope} \Delta g}{CA} \quad (3)$$

30 To determine ϵ with the detection chamber described in Figure 1 is used and the absorbance of a series of solutions with varying known concentrations are measured. By drawing an absorbance versus concentration curve, ϵ is determined with the equation (4) below with obtained slopeB.

$$\varepsilon = \frac{\text{slope}B}{L} \quad (4)$$

2. To determine the actual concentration of analyte in a reservoir water sample (C), the device consisting of the diffusive membrane layer and the binding layer is submerged in a water sample. After a period of time (t), the analyte concentration in the binding layer is measured using the detection chamber. The analyte concentration in the detection chamber (C₁) can be determined based on Beer's law (equation 5),

$$a = \varepsilon L C_1 \quad (5)$$

where absorbance (a) is proportional to absorptivity (ε), light passage length (L) and C₁ (provided as $\mu\text{g L}^{-1}$). As mentioned in #1, ε is determined using the same detection chamber with the same light passage length (L). The value is then used for calculation of C₁ (as indicated above)

3. As time increases, C₁ increases (due to diffusion). By measuring the C₁ value over a period of time t, the mass of the analyte in the preconcentration vessel (110) can be calculated and used to calculate C (the concentration of the analyte in the water body) based on the following equation (eq 1):

$$C = \frac{M \Delta m}{DA t}$$

where M is the mass accumulated after deployment for time t (M can be calculated via C₁ over time), A and Δm are exposure area of the device and thickness of the diffusive membrane, respectively. The actual concentration of analyte in the reservoir water sample (C; in $\mu\text{g L}^{-1}$) can then be determined.

To calculate the mass accumulated over a period of time, the following equation (6) is used:

$$M = C_1 * V \quad (6)$$

where V is the binding layer volume in the preconcentration vessel (110).

It will be appreciated that M can be replaced in equation (1) by C₁*V and that C₁ (the concentration of the analyte in the aqueous polymer solution) can subsequently be replaced by $a/\varepsilon L$ to provide equation (2).

$$C = \frac{a}{\epsilon b D} \frac{V \Delta m}{A t} \quad (2)$$

It will be appreciated that the concentration of the analyte in the open body of water may be calculated using either equation (1) or (2) based upon the values obtained for the various parameters as described herein.

Example 1:

As shown in Fig. 1, a quantitative preconcentration device was assembled by sealing a polypropylene tube containing 20 mL of an aqueous affinity polymer solution of polydiallyldimethylammonium chloride (PDA, molecular weight ~300,000) with a hydrated diffusive membrane (molecular weight cut off 12,000), having a thickness of 0.005 cm and a functional surface area of 2.57 cm². The membrane was clamped tightly by a rubber gasket with sure sealing. The device was submerged in an aqueous solution spiked with an analyte (analyte: 755 µg L⁻¹ (755 ppb) of phosphates). The phosphate in the spiked solution diffused through the membrane, was complexed by the polymer and so was trapped in the polymer solution and preconcentrated. The amount of phosphate preconcentrated in the polymer solution is proportional to its concentration in the spiked solution (Eq. 1).

After 24 h (t) of deployment, to measure the amount of phosphate preconcentrated in the polymer solution, a volume of 1.0 mL of the polymer solution was pumped out of the preconcentration device to the detection chamber and mixed with 0.2 mL of the colour reagent (0.14 mL of a solution containing 10% H₂SO₄, ammonium molybdate (0.044 M) and potassium antimonyl tartrate (2.9x10⁻⁴ M), and 0.06 mL of a solution containing ascorbic acid (0.1 M)) (Fig. 2). The resulting mixture was agitated/stirred for 8 minutes before the light absorbance of the mixed solution in the detection chamber was measured at 880 nm by the LEDs mounted on the top and bottom of the chamber and shown on the multi-meter (Fig. 2). Absorbance was calculated using the following equation,

$$\text{Absorbance} = \log(E_0/E),$$

where E (measured = 8.27 V) is voltage measured in the sample solution, and E₀ (measured = 268 V) is in a blank solution of the aqueous polymer (the polymer has no effect on light absorption), to provide an absorbance of 1.51.

The values of D (2.45 x 10⁻⁶ cm² s⁻¹ at 25°C) and ε (0.074 cm⁻¹ ppm⁻¹) were determined as described above. The volume of the polymer in the preconcentration vessel (110) was 20 mL.

Based upon the information above, the concentration of the analyte was calculated to be 4.1 ppm, which converts to a mass of 82 µg of phosphate in the 20 mL of polymer solution in the preconcentration vessel following 24 hours of deployment.

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Using the information above, the phosphate concentration in the spiked solution was calculated with Eq. 1 (as shown below). The detection chamber was then emptied to waste and cleaned.

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$$C = \frac{M\Delta m}{DA\epsilon t}$$

$$C = \frac{82.0 * 0.005}{2.45 * 10^{-6} * 2.57 * 24 * 3600}$$

$$C = 0.753 \text{ ppm}$$

The calculated value for the concentration in the spiked water was 0.753 ppm, which translates to 753 µg L⁻¹, which compares to the actual concentration of 755 µg L⁻¹.

The above combination of the preconcentration device and direct LED absorbance measurement provides a real time *in situ* system for monitoring of trace contaminants in fresh water.

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Example 2

Similar to example 1, 20 mL an aqueous polymer solution of poly(4-styrenesulfonate) (PSS) with molecular weight ~70,000 was used as the polymer solution in the sealed container with the same diffusive membrane (Fig. 1), but with an available surface area of 9.66 cm². The device was submerged in a solution containing an analyte (analyte 2: 100 µg L⁻¹ of arsenic).

The value for D and ε were 9.91x10⁻⁷ cm²/s at 25°C and 0.054 cm⁻¹ ppm⁻¹, respectively.

A volume of 1.0 mL polymer solution was pumped out of the above device to the detection chamber together with 0.1 mL of the colour reagent (Leuco Malachite Green; 0.05%) after 24 h deployment (Fig. 2). Light absorbance of the mixed solution in the detection chamber was measured at 617 nm by the LEDs mounted on the top and bottom of the chamber. The

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absorbance measured was 165 V, compared to the blank reading of 268 V, providing an absorbance of 0.21. The absorbance reading was used to calculate a concentration of 0.777 ppm for the analyte, which relates to a mass of 15.54 µg of analyte in 20 mL of said polymer solution.

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The arsenic concentration was then calculated using Eq. 1.

$$C = \frac{M\Delta m}{DA\epsilon t}$$

$$C = \frac{15.54 * 0.005}{0.99 * 10^{-6} * 9.66 * 24 * 3600}$$

$$C = 0.094 \text{ ppm}$$

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Thus, the calculated concentration of arsenic in the body of water is 94 µg L⁻¹, compared to an actual concentration of 100 µg L⁻¹, confirming the accuracy of the direct reading, with no need to separate the analyte from the binding layer.

CLAIMS

1. A preconcentration device for measuring the amount of a trace analyte in a water body, the device comprising:

5 a vessel having an opening;

a hydrated polymer membrane that covers the opening in the vessel; and

an aqueous solution of a polyelectrolyte polymer provided in the vessel and in direct contact with the membrane, wherein:

10 the polyelectrolyte polymer is polydiallyldimethylammonium chloride having a weight average molecular weight of from 200,000 Daltons to 350,000 Daltons; and

the polymer of the hydrated polymer membrane has a weight average molecular weight cut-off of 12,000 Daltons.

15 2. The preconcentration device of Claim 1, wherein the polymer of the hydrated polymer membrane is a hydrated cellulose polymer membrane.

3. The preconcentration device of Claim 1 or Claim 2, wherein the preconcentration
20 device further comprises a light absorbance detection unit, where the vessel is adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit.

4. The preconcentration device of Claim 3, wherein the light absorbance detection unit
25 comprises a detection chamber for containing the sample, a light emitting LED and a photodiode attached to a measuring unit, wherein the light emitting LED and the photodiode are arranged such that the light from the light emitting LED passes through the detection chamber before contacting the photodiode.

30 5. The preconcentration device of Claim 4, wherein the photodiode is a LED.

6. The preconcentration device of any one of the preceding claims, wherein the analyte is selected from one or more of the group selected from a phosphate, arsenic and an arsenate.

7. A method of analysing the amount of a trace analyte in a water body, wherein the method comprises the steps of:

(a) submerging a preconcentration device in a water body, the preconcentration device comprising:

5 a vessel having an opening;
a hydrated polymer membrane that covers the opening in the vessel;
and
an aqueous solution of a polyelectrolyte polymer provided in the vessel and in direct contact with the membrane;

10 (b) removing an aliquot of the aqueous solution of a polyelectrolyte polymer after a period of time has passed, and providing the same to a light absorbance detection unit comprising a detection chamber, a light emitting LED and a photodiode attached to a measuring unit, optionally the aliquot is obtained by removing the preconcentration device from the water body;

15 (c) adding a chemical reagent that reacts with the analyte to produce a colour before or after providing the aliquot of the aqueous solution to the detection chamber;

(d) measuring the light absorbance following reaction of the chemical reagent and analyte and calculating the concentration of the analyte in the water body,
20 wherein:

the polyelectrolyte polymer is polydiallyldimethylammonium chloride having a weight average molecular weight of from 200,000 Daltons to 350,000 Daltons; and

the polymer of the hydrated polymer membrane has a weight average molecular weight cut-off of 12,000 Daltons.

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8. The method of Claim 7, wherein the preconcentration device is adapted to enable a sample of the aqueous solution of a polyelectrolyte to be provided to the detection unit.

9. The method of Claim 7 or Claim 8, wherein the photodiode is a LED.

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10. The method of any one of Claims 7 to 9, wherein the analyte is selected from one or more of the group selected from a phosphate, arsenic and an arsenate.

11. An apparatus for analyte detection and/or measurement of a water body, comprising:
35 a floatable and/or a submergible vessel; and

the preconcentration device of any one of Claims 1 to 6, wherein the preconcentration device is adapted to enable at least the membrane of the preconcentration device to be in direct contact with water from the water body.