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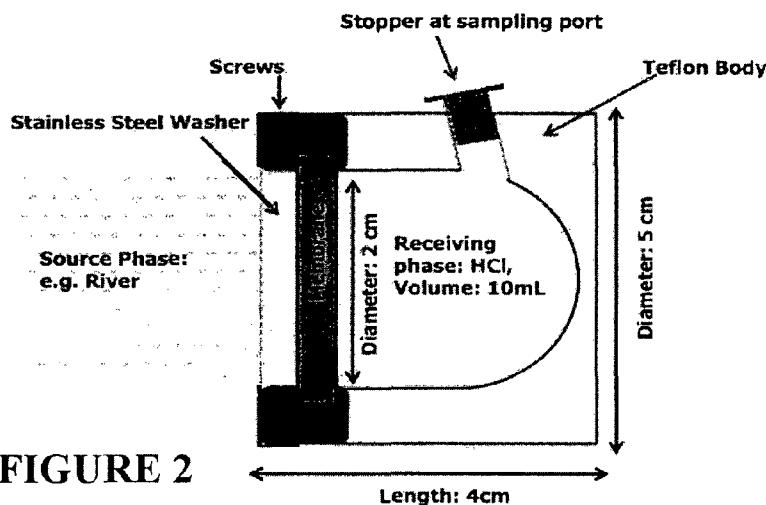
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(54) Title: DEVICE AND PROCESS FOR PASSIVE SAMPLING

**FIGURE 2**

(57) Abstract: The present invention generally relates to the field of monitoring or analysing an aqueous system (both water or sediment) for analytes and in particular to processes and devices for sampling and analysing the concentration or levels of specific analytes or solutes in an aqueous system such as a natural water system (e.g., rivers, ponds, etc) or industrial effluent streams. The analytes or solutes may or may not be pollutants of said aqueous systems. The sampling device comprises a polymer inclusion membrane or a composite polymer inclusion membrane.

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DEVICE AND PROCESS
FOR
PASSIVE SAMPLING

5

FIELD

The present invention generally relates to the field of monitoring or analysing an aqueous system (both water or sediment) for analytes and in particular to processes and devices for
10 sampling and analysing the concentration or levels of specific analytes or solutes in an aqueous system such as a natural water system (e.g., rivers, ponds, etc) or industrial effluent streams. The analytes or solutes may or may not be pollutants of said aqueous systems.

15

BACKGROUND

Sampling technologies in environmental analysis are gaining more importance these days as the presence of certain chemicals in the environment, which includes the air, soils, and waters, can have adverse effects on organisms including humans. Passive sampling, which is the sampling over a long period of time (e.g. from days to many months), is a simple and
20 low cost technology that allows the sampling of a huge array of chemicals at numerous locations. It also allows the determination of the average concentration of bio-available analytes over time, which is not possible with spot sampling due to their ever-fluctuating concentrations in nature and/or episodic contamination. This approach also allows the study of the uptake and accumulation of chemicals (e.g. metals, and organic pollutants) in
25 organisms.

A number of passive samplers for sampling of various chemical species in water (mainly metallic and organic species) have been developed. In many of them the sampling process is based on passive dialysis where the analyte diffuses across a semipermeable hydrophilic
30 porous membrane into a receiver aqueous solution until equilibrium is reached. Such passive samplers do not need complex pretreatment steps for the analysis of the receiver

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phase. However, passive dialysis has limited selectivity, determined by the pore size of the membrane. This process has no preconcentration capabilities which is often crucial for the detection of contaminants at trace levels. These deficiencies have been overcome to some extent by the introduction of chelating resins to the receiver aqueous phase or by replacing

5 the porous hydrophilic membrane with a supported liquid membrane (SLM) and adding a suitable stripping reagent (e.g. complexing agent) to the aqueous receiver phase. SLMs are macroporous hydrophobic membranes impregnated with an organic solution of the extractant (membrane liquid phase) which is retained in the membrane pores by capillary forces. A passive sampling device operating on similar principles is the diffusion gradient

10 in thin-film (DGT) sampler. This sampler consists of a gel layer incorporating a compound that strongly binds the analyte. The gel layer is separated from the aquatic environment by a hydrated acrylamide diffusion gel. In the case of DGT and chelating resin devices a series of pretreatment steps (e.g. extraction, desorption) are required prior to the analytical measurement of the preconcentrated analyte. These analytical procedures

15 require a laboratory environment and cannot be conducted on-site. The analysis of the aqueous receiver phase in SLM-based passive samplers is often straightforward. However, SLMs have limited lifetime due to the leaching of the membrane liquid phase into the aquatic environment and the receiver phase.

20 The present invention seeks to overcome at least some of the shortcomings of known sampling devices and processes.

SUMMARY OF THE INVENTION

25 The present invention provides devices and processes for passive sampling of analytes or solutes in an aqueous system through the utilisation of polymer inclusion membranes (PIMs) as ion exchange membranes which can effectively and often selectively extract said analytes or solutes from the aqueous system.

30 Accordingly, in an aspect the invention provides devices for passive sampling of an aqueous system wherein the passive sampling device comprises a polymer inclusion

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membrane (PIM) or a composite-polymer inclusion membrane.

In an embodiment the device for passive sampling of an aqueous system comprises:

- (i) a receptacle;
- 5 (ii) sampling aperture; and
- (iii) a membrane which is a polymer inclusion membrane or a composite-polymer inclusion membrane (PIM);

wherein

- 10 (a) the receptacle contains a receiver solution and is fitted with the sampling aperture to allow for the addition or removal of the receiver solution from said receptacle, and
- (b) the membrane is in fluid communication with both the receiver solution and the aqueous system.

- 15 In an embodiment the membrane is attached to the receptacle.

In an embodiment the membrane is a polymer inclusion membrane.

- In another embodiment the membrane is a composite-PIM, wherein that the composite-
- 20 PIM is characterised with a layer of a non-PIM polymer.

- In a further aspect the present invention provides a process for passive sampling of an aqueous system including the step of immersing a passive sampling device into said aqueous system wherein the passive sampling device comprises a polymer inclusion
- 25 membrane or a composite-polymer inclusion membrane.

- In a further aspect the present invention provides a process for passive sampling of an aqueous system including the step of transferring a flow of water through a passive sampling device wherein the passive sampling device comprises a polymer inclusion
- 30 membrane (PIM) or a composite-polymer inclusive membrane and whereby the flow of water comes into contact with the PIM or composite-PIM.

In an embodiment the above two aspects include a detection step.

BRIEF DESCRIPTION OF THE DRAWINGS

- 5 **Figure 1.** Schematic of a membrane-based passive sampler according to the invention.
- Figure 2.** Schematic diagram of the Zn(II) passive sampler according to the invention.
- Figure 3.** Transient Zn(II) concentration in the receiver solution in the case of 0 (◆), 100 $\mu\text{g L}^{-1}$ (■), and 500 $\mu\text{g L}^{-1}$ (□) Zn(II) concentration in the external solution.
- 10 **Figure 4.** Calibration curve using electrothermal atomic absorption spectrometry (ET-AAS).
- Figure 5.** Emission intensity versus volume ratio of the sample (50 $\mu\text{g L}^{-1}$ Zn(II)) and reagent (160 μM p-taq in 0.19 M SDS and 0.45 M Tris-HCl buffer, pH7.5) solutions.
- 15 **Figure 6.** Calibration curve for the fluorimetric measurement of Zn(II) in deionized water.
- Figure 7.** Calibration curve for the fluorimetric measurement of Zn(II) in 0.1 M HCl solution.
- Figure 8.** Transient Zn(II) concentration in the receiver solution in the case of 0 $\mu\text{g L}^{-1}$ (○), 25 $\mu\text{g L}^{-1}$ (●), 50 $\mu\text{g L}^{-1}$ (▲), 75 $\mu\text{g L}^{-1}$ (◆), and 100 $\mu\text{g L}^{-1}$ (■) Zn(II) concentration in the external solution (PIM: 40 % D2EHPA/60 % PVC (m/m)).
- 20 **Figure 9.** Average rate of Zn(II) extraction in the passive sampler in relation to the time-weighted average bulk Zn(II) concentration.
- 25 **Figure 10.** Calibration curves for the passive sampler for 4, 8 and 10 days of sampling.
- Figure 11a.** Photograph of a membrane-based passive sampler according to the invention.
- Figure 11b.** Photograph of components of the passive sampler in the order of assembly: (a) Stainless steel frame, (b) Teflon block with receiving well and sampling port, (c) PIM cut to a square with each side being 2.5 cm, (d) Gore-tex™

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washer, (e) Sheet Teflon washer, (f) Stainless steel washer, (g) Stainless steel washers and bolts, and (h) Stopper for the sampling port.

Figure 12. Graph depicting NH_4^+ concentration (mgL^{-1}) as a function of time (h).

Figure 13. Schematic of a membrane-based passive sampler according to the invention for NH_4^+ sampling.

Figure 14. Photograph of a membrane-based passive sampler according to the invention for NH_4^+ sampling.

Figure 15. Schematic of a gas-diffusion flow injection analysis (GD-FIA) system for ammonium monitoring (Reagents: 2 M NaOH; cresol red/thymol blue as the indicator; PP, peristaltic pump (flow rate 1 mL min⁻¹); IV, injection valve (sample 200 mL); MC, mixing coil (50 cm long); GDU, gas-diffusion unit (Teflon membrane); l, spectrophotometric flow-through cell (580 nm); w, waste).

Figure 16. Graph depicting NH_4^+ concentration (mgL^{-1}) as a function of time (h).

Figure 17. Graph depicting NH_4^+ concentration (in receiver solution) vs NH_4^+ concentration (in feed solution) (both mgL^{-1}).

Figure 18. Schematic diagram of the flow-through passive sampler according to the invention.

Figure 19. Photographs of a modified stainless steel washer (left) and the assembled flow-through passive sampler (right) of the invention.

Figure 20. Schematic diagram of the flow-through passive sampling system of the present invention incorporating a pump, analyte source, and waste repository.

DESCRIPTION OF THE INVENTION

Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

The reference in this specification to any prior publication (or information derived from it),

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or to any matter which is known, is not, and should not be taken as an acknowledgment or admission or any form of suggestion that prior publication (or information derived from it) or known matter forms part of the common general knowledge in the field of endeavour to which this specification relates.

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The present invention is predicated on the discovery that analytes and solutes which may be present in, for example, natural aquatic systems (including both water or sediment) or effluent industrial streams, can be efficiently (and often selectively) extracted with the use of PIMs which are characterised by having an immobilised extractant (such as a quaternary ammonium salt) and as such, may be effective membranes for the passive sampling of said analytes and solutes in an aqueous (e.g., water) system.

Nature of the PIM

15 Polymer inclusion membranes are known in the art, and may also be referred to as "polymer liquids", "gelled liquids", "polymeric plasticized", "fixed-site carriers" or "solvent polymeric membranes". The main advantage of PIM's over, for instance, supported liquid membranes (SLMs) is their stability. Also, unlike bulk liquid membranes (BLMs), PIMs are generally not characterised as having low interfacial surface areas and mass transport rates. PIMs also do not suffer the problem of emulsion breakage which tends to plague emulsion liquid membranes (ELMs).

PIMs according to the present invention are generally formed by mixing (casting) a solution which contains an analyte/solute extractant (e.g. a quaternary ammonium salt), a plasticizer/modifier (optional) and a base polymer. The casting process is typically facilitated with the use of organic solvents (such as ethers (e.g., THF, diethylether)) and chlorinated solvents (e.g., dichloromethane)), which are typically removed during membrane formation (e.g. by air drying or *in vacuo*).

30 It will be appreciated that the "extraction" and "back-extraction" processes referred to herein involve the controlled transport of a desired or target analyte/solute into and out of

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the membrane. Such processes are facilitated, in part, by a carrier (referred to herein as the "extractant") that is essentially an analyte/solute complexing agent or an ion-exchanger which is immobilised in the PIM.

- 5 In an embodiment the extractant constitutes from 5 – 40% m/m of the PIM, in another embodiment from about 10% - 30% m/m and in a further embodiment from about 15 – 25% m/m of the PIM.

In an embodiment where the PIM is intended to be used in a passive sampler for
10 monitoring ammonia (present as NH_3 and NH_4^+), the extractant is DNNSA or its salts (e.g. potassium or sodium salt) and may comprise 10-30% of the total composition (% m/m) of the PIM.

In an embodiment the DNNSA is utilised as a 0.2 M – 0.5 M solution in an organic solvent
15 such as heptane. Such a solution may constitute from about 40-15% m/m of the total PIM composition. Alternatively purified DNNSA where the heptane has been removed or a salt of DNNSA can be employed.

In an embodiment where the PIM is intended to be used in a passive sampler for
20 monitoring zinc(II) the extractant is D2EHPA and may comprise 30-50% (for example about 40%) of the total composition (% m/m) of the PIM.

Examples of suitable extractants and typical target analytes/solutes are listed in Table 1:

Table 1: Examples of PIM carriers (extractants) and their typical target solutes (All
25 abbreviations are explained in the *Glossary of Terms* section).

Type of carriers/extractants	Examples	Target solutes/analytes
Sulphonic acids and their salts	DNNSA and its salts	$\text{NH}_4^+/\text{NH}_3$

Type of carriers/extractants	Examples	Target solutes/analytes
Quaternary amines	Aliquat 336	As(V), Au(III), Cd(II), Cr(VI), Cu(II), Pd(II), Pt(IV), small saccharides, amino acids, lactic acid
Tertiary amines	TOA Other tri-alkyl amines	Cr(VI), Zn(II), Cd(II), Pb(II)
Pyridine & derivatives	TDPNO	Ag(I), Cr(VI), Zn(II), Cd(II)
Hydroxyoximes	LIX [®] 84-I	Cu(II)
Hydroxyquinoline	Kelex 100	Cd(II), Pb(II)
β -diketones	Benzoylacetone Dibenzoylacetone Benzoyltrifluoroacetone	Sc(III), Y(III), La(III), Pr(III), Sm(III), Tb(III), Er(III), Lu(III)
Alkyl phosphoric acids	D2EHPA D2EHDTA	Pb(II), Ag(I), Hg(II), Cd(II), Zn(II), Ni(II), Fe(III), Cu(II)
Carboxylic acids	Lauric acid Lasalocid A	Pb(II), Cu(II), Cd(II)
Phosphoric acid esters	TBP	U(VI)
Phosphonic acid esters	DBBP	As(V)
Others	CMPO, TODGA, TOPO, polyethylene glycol	Pb(II), Cd(III), Cs ⁺ , Sr(II)
Crown ethers and Calix arenes	DC18C6 BuDC18C6	Na ⁺ , K ⁺ , Li ⁺ , Cs ⁺ , Ba(II), Sr(II), Pb(II), Sr(II), Cu(II), Co(II), Ni(II), Zn(II), Ag(I), Au(III), Cd(II), Zn(II), picrate
Others	Bathophenanthroline Bathocuproine	Lanthanides

In an embodiment the passive sampling devices of the present invention are useful for the sampling of heavy metals (e.g. Hg(II), Zn(II), Cu(II), Cd(II), Pb(II), U(VI), Cr(VI)); toxic inorganic ions and nutrients (e.g., ammonium (NH₄⁺), cyanide (CN⁻), thiocyanate (SCN⁻), arsenate (AsO₄³⁻), arsenite (AsO₂⁻) or (AsO₃³⁻), phosphate (PO₄³⁻) and nitrate (NO₃⁻); and small organic ions (e.g. some pesticides and herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D) and simazine).

The PIM according to the present invention may be formed from any suitable base

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polymer which provides mechanical strength to the membrane.

In one embodiment the polymer is selected from poly(vinyl chloride) (PVC), cellulose triacetate (CTA), cellulose tributyrate (CTB), PVDF and PVDF co-polymers, or suitable
5 derivatives thereof.

In an embodiment the polymer is PVC, CTA or a derivative thereof.

In an embodiment the polymer is PVC.
10

In an embodiment the polymer constitutes from about 40-80% m/m of the PIM, in another embodiment from about 50-75% m/m, in a further embodiment from about 77-75% m/m, and still in a further embodiment about 70% m/m.

15 For instance, where the analyte is Zn(II) the polymer may be PVC comprising about 50-70% (m/m), and preferably about 60% (m/m) of the total PIM composition.

In an embodiment where the analyte is ammonia (present as NH_3 and NH_4^+), the polymer may be PVC comprising also around 50-70%, and preferably about 60% (m/m) of the total
20 PIM composition.

The PIM also may comprise a plasticizer or modifier component. The role of the plasticizer is to penetrate between polymer molecules and to "neutralize" the polar groups of the polymer with its own polar groups or to merely increase the distance between the
25 polymer molecules and hence reduce the strength of the intermolecular forces. Accordingly, the plasticizer may be any suitable organic compound which is able to function as described above. Suitable organic compounds include those containing a hydrophobic alkyl backbone with one or several highly solvating polar groups. The role of the modifier is to increase the solubility of the extracted chemical species in the membrane
30 liquid phase.

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In an embodiment the plasticizer/modifier is selected from the group consisting of 2-nitrophenyl octyl ether (2-NPOE), dibutyl butyl phosphonate (DBBP), 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-dodecanol, 1-tetradecanol, o-nitrophenylpentyl ether (oNPPE), tributylphosphate (TBP), dioctylphthalate (DOP), bis(2-ethylhexyl)terephthalate (DDTP), dioctylsebacate (DOS), and tri-(2-ethylhexyl)phosphate(T2EHP).

In an embodiment the plasticizer is selected from TBP, 2-NPOE, 1-tetradecanol, and 1-dodecanol.

10

In an embodiment the plasticizer/modifier constitutes from about 0-40% m/m of the PIM, preferably about 0 – 30% m/m and more preferably from about 0-15% m/m.

In an embodiment the PIM for Zn(II) sampling does not comprise a separate plasticizer/modifier since D2EHPA can also act as a plasticizer.

15

In another embodiment, for the passive sampling of ammonia (present as NH_3 and NH_4^+) the PIM comprises 1-dodecanol or 1-tetradecanol as a modifier. In relation to this embodiment the modifier may comprise 0-30% of the total PIM composition.

20

The skilled person would appreciate that the PIMs of the present invention may also include additional components to aid in the extraction process. For instance, the PIMs may include extractants other than, for instance, D2EHPA (in Table 1), plasticizers/modifiers and base polymers, antimicrobial agents (for instance, to inhibit membrane fouling), antioxidants (for increased stability), porosity agents (porogens), ferromagnetic particles, and residual amounts of casting solvents.

25

The membrane according to the present invention may also be a composite – PIM, to further improve the performance of PIM-based separation. For instance, a composite – PIM may characterised as a PIM with an attached non-PIM polymer layer such as Nafion® or a microporous membrane layer (e.g. cellulose acetate or triacetate). Preferably, the non-

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PIM polymer layer of such a composite will be exposed to the external aqueous system (the PIM exposed to the receiver solution). Such an arrangement is predicated to drastically reduce any leaching of the PIM liquid phase into the aqueous system thus improving the stability of the PIM layer. At the same time the non-PIM polymer layer will provide mechanical protection to the PIM layer. The loss of PIM liquid phase is strongly dependent on the ionic strength and pH of the aqueous solution in contact with the membrane. High ionic strength and low pH reduce to a minimum or even practically eliminate the leaching of acidic extractants (e.g. D2EHPA) by: (1) preventing their dissociation (the extractant anion is generally more soluble in water than the corresponding neutral molecule); and (2) the so-called 'salting out effect' which decreases the solubility of organic compounds in aqueous solutions. The receiver solution in the proposed passive sampler is preferably of small volume (i.e. several mL) and typically of high acidity. These conditions will practically eliminate the leaching of the acidic extractant into it. The external aqueous system (e.g. river, pond, etc) is of much larger volume and may be of relatively high pH (i.e. 6.5 - 9.0). These conditions will facilitate the leaching of acidic extractants and therefore the introduction of a non-PIM polymer layer is expected to minimize or practically eliminate this unwanted process. An additional benefit of using composite-PIM membranes will be the higher degree of control over the rate of membrane mass transfer of a solute such as ammonia. The transport rate across Nafion[®] and dialysis membranes is relatively high compared to PIMs and more difficult to control. It may happen to be too high for some passive sampling applications. By introducing the PIM layer of controllable thickness and composition, it will be possible to manipulate the overall composite membrane permeability to suit the corresponding passive sampling requirements.

25

The Passive Sampler and Sampling Process

An example of a device for passive sampling is shown in **figure 1**. This figure depicts a housing (1) (or receptacle) defining a cavity (2) for the receiver solution, the cavity having an opening (3) spanned by a membrane (4) which is a polymer inclusion membrane or a composite-polymer inclusion membrane, wherein the membrane includes an inner surface

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(5) which is contactable with the receiver solution and an outer surface (6) which is contactable with the aqueous system (which can be water or sediment) such that the membrane is in fluid communication with the receiver solution and the aqueous system. The housing or receptacle also includes a sampling part (7) for addition or removal of the receiver solution to or from the cavity or receptacle. As shown in **figure 1** the sampling port may extend from the housing. The membrane may be affixed to the housing by a sealing device. The sealing device may include, in an embodiment, at least one gasket. The at least one gasket may comprise a polymeric material.

10 The sampling process involves contacting a device with an aqueous system such that the PIM or composite-PIM is exposed to the aqueous system (e.g. water or sediment) to be sampled. This may simply involve immersing the device in the aqueous system. Such devices are referred to herein as 'dip-in' passive sampling devices. As an alternative sampling procedure the present invention also contemplates 'flow-through' sampling devices in which the device is modified to allow for the PIM or composite-PIM to contact a flow of liquid from the aqueous system (e.g. water) to be sampled.

In an embodiment this modification may include the addition of a cell compartment which is connected to the housing or receptacle and encloses the outer surface of the PIM and accommodates a flow of liquid from the aqueous system (e.g. water) such that the PIM is exposed on one side to the receiving fluid and on the other side the flow of liquid. Such a cell compartment may be described as a flow-through cell and may be coupled to the housing for flow of liquid from the aqueous system over the outer surface of the membrane.

25

Accordingly, in a further aspect the invention provides a device for flow-through passive sampling of an aqueous system comprising:

- (i) a receptacle containing a receiver solution;
- (ii) a cell compartment containing the aqueous system;
- 30 (iii) a sampling aperture which is fitted to the receptacle to allow for the addition or removal of the receiver solution from said receptacle,

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wherein:

- (a) the cell compartment is connected to the receptacle whereby the receiver solution and the aqueous system are separated by a membrane which is a polymer inclusion membrane (PIM) or a composite-PIM being in fluid communication with the receiver solution by its inner surface and also the aqueous system by its outer surface, and
- (b) the cell compartment comprises an inlet and outlet to allow a flow of liquid from the aqueous system to contact the outer surface of the PIM or composite-PIM.

10

The present invention provides a novel passive sampling approach involving intermittent measurement of, for instance, a preconcentrated contaminant without removing the passive sampler from the aqueous system. This is done, for instance, by immersing the device of the present invention into the aqueous system which may be a natural water stream (such as river, pond, well, etc), an industrial water stream (such as an evaporation pond, industrial waste water or effluent stream, etc) or sediment of an aqueous system. Thus, it will be possible to collect incremental time averaged concentrations of the analyte/solute or contaminant ('dynamic sampling') using the same passive sampling device as opposed to classical passive sampling where an average contaminant concentration for the entire sampling period can only be provided. Therefore, this new approach will lead to more timely management response to, for instance, contamination events.

Currently used passive sampler devices allow the assessment of the average concentration of the contaminant of interest over the entire deployment period. In most cases this information can only be obtained after the sampler has been transported to an analytical laboratory. Often complex analytical pretreatment (e.g. extraction, desorption) prior to the contaminant measurement is required. The present sampler devices have the significant advantage in that they are low-cost reusable passive samplers, employing extracting membranes. Unlike existing passive samplers, the present sampling devices will allow both conventional passive sampling and 'dynamic sampling'.

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During the sampling process the analyte/solute is collected in a receiver aqueous phase ('receiver solution') where it can be measured both intermittently and at the end of the deployment period. Preferably the receiver solution is a dilute aqueous acid solution but it could be a solution of a suitable salt. The present passive samplers are easy to use and
5 adapt to various contaminants by selecting suitable extracting membranes and chemical compositions of the receiver aqueous solutions.

By varying the membrane composition in addition to the composition of the receiver solution it will be possible to control the rate of membrane mass transfer of the target
10 chemical species. This will allow one to select a rate which is appropriate for the duration of the sampling period and the expected concentration of the target chemical species. In this way, situations involving the saturation of the receiver solution with the target chemical species can be avoided.

15 The extractant agents in the receiver solution should be capable of either complexing the analyte and thus back-extracting it from the membrane or by exchanging with the analyte in the membrane. For example Zn^{2+} and UO_2^{2+} in a D2EHPA/PVC membrane can be back-extracted into an acidic solution as a result of the dissociation of the corresponding complexes in the membrane and ion-exchange between these 2 ions in the membrane and
20 the H^+ ions in the receiver solution. The thiocyanate anion (SCN^-) can be back-extracted from an Aliquat 336/PVC membrane by NaNO_3 as a result of the ion-exchange between the SCN^- and NO_3^- anions at the membrane solution interface. Similarly, the ammonium cation extracted into a DNNSA/PVC membrane can be back-extracted into a solution of an acid or salt (e.g. KCl) as a result of the interfacial ion-exchange between NH_4^+ on one
25 hand and H^+ or another cation (e.g. K^+) on the other.

Analysis of the Receiver Solution - monitoring

The concentration of the analyte or solute transferred from the aqueous system into the
30 receiver solution may be achieved by quantitative and qualitative methods known in the art. This may involve the utilization of analytical methods such as differential pulse anodic

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stripping voltammetry, atomic absorption spectrometry, spectrophotometry, and/or fluorimetry. It would be appreciated that in the device mentioned herein the sampling of the receiver solution at any point of this may be achieved through the sampling aperture. The analysis of the receiver solution can be performed in a laboratory by suitable analytic methods such as those mentioned above or on-site by portable analyzers. Examples of such devices are analyzers utilizing flow analysis techniques, ion-selective electrodes, or paper-based microfluidics.

The invention will now be further described with reference to the figures and the following non-limiting examples. However, it is to be understood that the particularity of the following description of the invention is not to supersede the generality of the preceding description of the invention.

Examples

1. Passive Sampling of Zn(II)

The aim is to investigate the use of PIMs in passive samplers for sampling Zn(II) in natural waters. A sampling device that comprises a PIM was designed, made, and modified to allow the investigations to take place in both synthetic solutions and natural waters.

Experimental

Reagents

The commercial extractant D2EHPA (Sigma-Aldrich), PVC (High Molecular Weight) (Selectophore, Fluka, Switzerland), THF (AR, Chem-Supply, Australia) and sodium dodecyl sulfate (SDS) (Scharlau Chemie, Australia) were used as received.

Zinc(II) solutions of 0-100 $\mu\text{g L}^{-1}$ in water were prepared from a stock solution of 100 mg L^{-1} of Zn(II) (ZnCl_2 , Unilab, Australia). Standards containing 0 – 125 $\mu\text{g L}^{-1}$ Zn(II) in water and 0 – 10000 $\mu\text{g L}^{-1}$ Zn(II) in 0.1 M HCl (Scharlau Chemie, Australia) were

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prepared from stock solutions of $1000 \mu\text{g L}^{-1}$ and 100 mg L^{-1} of Zn(II), respectively, when required.

The receiver solution of 0.1 M HCl was prepared by appropriate dilutions of the supplied
5 concentrated acid (Scharlau Chemie, Australia).

Buffer for anodic stripping voltammetry: A solution of 1.42 M acetate buffer, pH 4.3, was prepared by dissolving 56.8 g of acetic acid (Chem-Supply, Australia) and 32.8 g of sodium acetate trihydrate (Chem-Supply, Australia) in water and making up to 1 L.

10

Preparation of p-tosyl-8-aminoquinoline (p-taq) as a fluorescent reagent: The method of preparation is similar to the one described by Billman et al (1962). 0.86 g (6 mmole) of 8-aminoquinoline was dissolved in 10 mL of pyridine in a 25 mL conical flask by stirring in an ice-water bath. 1.14 g (6 mmole) of p-tosylchloride was added in small amounts over 2
15 hours with the solution being stirred throughout. The reaction mixture was then poured into 40 mL of cold water with vigorous stirring. A pink solid separated out, and was filtered and washed with water, and then recrystallised with ethanol. This yields a product of p-taq, which appeared as off-white crystalline needles (1.24 g, 69%).

20 Preparation of the p-taq reagent: Stock solutions of p-taq were made up in 60/40 (v/v) ethanol-water mixtures, and heated to 50°C to ensure complete dissolution when preparing working solutions.

Stock solutions of 0.4 M SDS were prepared by dissolving the appropriate amount of SDS
25 in water and stirring until all the solid had dissolved.

Stock solutions of Tris-HCl buffer were prepared by dissolving the appropriate amount of solid Tris (Chem-Supply, Australia), in water and titrating until the desired pH was reached.

30

- 17 -

A working reagent solution of p-taq was obtained by mixing 100 mL of the stock p-taq solution with 450 mL of SDS, and 450 mL Tris-HCl, pH7.5, to yield a mixture consisting of 160 μ M p-taq, 0.19 M SDS, and 0.45 M Tris-HCl.

- 5 Deionized water (18.2M Ω cm, Millipore, Synergy 185, France) was used in the preparation of all solutions.

Apparatus

- 10 All glassware was soaked for at least 24 hours in 10% HNO₃ (Scharlau Chemie, Australia), and washed thrice with deionized water prior to use.

Bulk solutions of Zn(II) were circulated using small water feature pumps (AQUAP333L, Watermaster, White International Pty Ltd, Australia).

- 15 Anodic Stripping Voltammetry measurements were carried out using an electrochemical analyser (797VA Computrace, Metrohm, Switzerland).

Atomic Absorption Spectrometry (AAS) measurements were carried out using a polarized Zeeman atomic absorption spectrophotometer (Model Z-2000, Hitachi, Japan).

20

Fluorescence spectroscopy measurements were carried out using a fluorescence spectrometer (Cary Eclipse, Varian Inc.).

Design of 'Dip-In' Passive Sampler

- 25 A schematic diagram of a 'dip-in' passive sampler (Fig. 2, also see photograph – Fig. 11a) is similar to the generic design shown in Fig. 1. Figure 11b shows the components (unassembled) of the passive sampler device. It incorporates a PIM as a barrier between the bulk source phase (i.e. aqueous system) and an internal receiver solution. This receiver solution is contained in a well ('receptacle') of 10 mL that is cut into a 50 mm diameter
30 block of Teflon, with an angled sample port ('sampling aperture') as shown, to allow intermittent sampling as part of the research. The PIM is placed at the mouth of the well

- 18 -

and secured by another Teflon and stainless steel washer, and screwed down until it is firm.

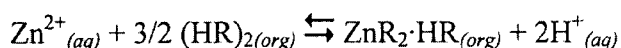
Experimental Procedures

- 5 Membrane preparation: A known mass of PVC was added to a solution of D2EHPA of known mass and THF (10 mL per g of total membrane mass) and stirred until dissolved. The resulting solution was then pipetted into glass rings placed on glass plates, and covered with a piece of filter paper and a watch glass, and left to stand for two days until all the solvent evaporated. The membrane could then be obtained by peeling it off the
10 glass ring after dropping a few drops of 0.1M HCl onto its sides.

- Preliminary experiments: The passive samplers were set-up, incorporating 40% D2EHPA/PVC (m/m) PIMs, with a receiver solution of 10 mL of 0.1 M HCl. These passive samplers were placed in tubs containing 10 L of 0, 100, and 500 $\mu\text{g L}^{-1}$ of Zn(II).
15 Samples of 0.5 mL of the receiver solution were taken at pre-determined periods of time (with replacement of fresh 0.1 M HCl) and diluted to 10 mL. The resulting samples were then analysed by anodic stripping voltammetry.

The extraction and back-extraction of Zn^{2+} can be described by the following equation:

20



- where $(\text{HR})_2$ refers to the dimeric form of D2EHPA that acts as a cation exchanger and the subscripts (aq) and (org) refer to species present in the aqueous and organic phases,
25 respectively.

Anodic Stripping Voltammetry (ASV): 5 mL of Zn(II) samples were added to 5 mL of 1.42 M acetate buffer, pH 4.3, and the mixtures were analysed.

- 30 Other analytical methods were also tested and used in the subsequent experiments.

- 19 -

Electrothermal Atomic Absorption Spectrometry (ET-AAS): 30 μL of Zn(II) samples were analysed by injecting them into the graphite furnace of the spectrometer.

5 Fluorescence spectroscopy: As a start, 1.5 mL of Zn(II) samples were added to 1.5 mL of the p-taq reagent and its emission intensity recorded at 503 nm with an excitation wavelength of 377 nm. Various parameters were investigated to optimise the sensitivity of the determination.

Calibration: The passive samplers were set-up, incorporating 40% D2EHPA/PVC (m/m)
10 PIMs, with a receiver solution of 10 mL of 0.1 M HCl. These passive samplers were placed in tubs containing 10 L of 0, 25, 50, 75, and 100 $\mu\text{g L}^{-1}$ of Zn(II). Samples of the receiver solutions were taken at pre-determined periods of time (with replacement of fresh 0.1 M HCl). The external bulk concentration was also monitored, by taking samples without replacement. The bulk concentration was maintained constant by adding small
15 volumes of 100 mg L^{-1} of Zn(II) solution when the concentration decreased by more than 3 $\mu\text{g L}^{-1}$ due to Zn(II) extraction by the passive sampler. Both the receiver and the external solutions were analysed in duplicate by the fluorimetric method outlined above.

Results and Discussion

20 Preliminary experiments

The preliminary experiments over a sampling period of 12 days have shown a substantial preconcentration of Zn(II) in the receiver solution (Fig 3).

Analytical methods

25 Anodic Stripping Voltammetry (ASV)

Due to the time-consuming nature of ASV (sampling rate $\sim 10 \text{ h}^{-1}$) combined with an analogue trace output, other methods for trace Zn(II) determination were explored in an attempt to reduce the analysis time and increase the efficiency and reproducibility of analysis. In addition, large dilutions of the receiver solution had to be done in the case of
30 ASV analysis to decrease the acidity of the sample so it could be buffered by the acetate

- 20 -

buffer, and also to provide the volume that were required for the analysis (5 mL). These large dilutions were an additional source of contamination.

Electrothermal Atomic Absorption Spectrometry (ET-AAS)

- 5 ET-AAS was trialled as an analytical method due to its sensitivity and usage of small sample volumes of less than 100 μL . However, for Zn(II) standards in water, the linear range was found to be up to 2 $\mu\text{g L}^{-1}$ of Zn(II) (Fig. 4), which again required an undesirably high dilution of the original samples with the associated contamination issues.

10 **Fluorimetry**

Fluorimetry, using p-taq as a reagent, reported to be a sensitive method for the determination of Zn(II) in flow injection analysis, was trialled as a batch analytical method in the present study.

15 *Optimisation of the fluorimetric method:*

Various reagent: sample volume ratios were tested on a standard containing 50 $\mu\text{g L}^{-1}$ of Zn(II), and the results are shown below in Fig. 5.

- Fig. 5 shows that the emission increases in excess of p-taq, i.e. small volume ratios. This is attributed to the fluorescence emission of the Zn(II)-p-taq complex being much larger as compared to that of p-taq alone. However as the reagent: sample volume ratio increases, the background fluorescence of p-taq also increases and becomes high compared to the fluorescence of the Zn(II)-p-taq complex. A reagent: sample volume ratio of 0.33 was chosen (i.e. 2.25 mL sample + 0.75 mL reagent) as the optimal value of this parameter.

25

Other parameters

Other instrumental parameters such as the excitation and emission slit widths (which were kept equal), and the photomultiplier tube (PMT) voltage were also investigated (Table 2).

- 30 **Table 2:** Influence of various instrumental parameters on the emission intensity of a 50 $\mu\text{g L}^{-1}$ Zn(II) sample and 160 μM p-taq reagent mixture.

- 21 -

		PMT voltage (V)		
		400	600	800
Slit width (nm)	5	0.08	6.28	83.98
	10		64.22	847.5

Although a high photomultiplier tube voltage and large slit width provided the highest sensitivity it was decided to select 600 V tube voltage and 10 nm slit width as the optimal values to eliminate the need of substantial dilution of the samples.

A calibration curve constructed under optimal conditions is shown in Fig 6.

Analytical figures of merit

The calibration curve shown in Fig. 6 is linear in the concentration range of 10-200 $\mu\text{g L}^{-1}$ Zn(II). The detection limit, defined as the concentration corresponding to emission intensity three times the standard deviation of the blank, was found to be 1 $\mu\text{g L}^{-1}$. Five replicate measurements yielded a relative standard deviation (RSD) of 1.2 %. The sampling rate was found to be 60 h^{-1} .

Adapting the analytical method for Zn(II) determination to the determination of Zn(II) in acidic solutions

It was important to adapt the method to acidic solutions to allow its use for the determination of Zn(II) in 0.1 M HCl receiver solutions. A modified p-taq reagent mixture was prepared by adding 10 mL of the p-taq stock solution to 450 mL of 0.4 M SDS and 450 mL of 0.2 M Tris-HCl buffer (pH 8.3), and making to 1 L with deionized water. The solution thus obtained contained 16 μM p-taq in 0.19 M SDS and 0.09 M Tris-HCl buffer (pH 8.3). The analytical procedure involved the addition of 3 mL of the 16 μM p-taq reagent solution to 0.1 mL of a Zn(II) solution in 0.1 M HCl. The corresponding calibration curve is shown in Fig. 7.

Analytical figures of merit

The calibration curve shown in Fig. 7 is linear in the concentration range of 400-10,000 $\mu\text{g L}^{-1}$ Zn(II) in 0.1 M HCl. The detection limit was found to be 120 $\mu\text{g L}^{-1}$. This method was used for all future determinations of Zn(II) in the acidic receiver solution of the passive sampler.

Passive sampler calibration

Passive sampling was conducted in external solutions with Zn(II) concentration in the range 0 to 100 $\mu\text{g L}^{-1}$. The corresponding transient Zn(II) concentrations in the receiver solution are shown in Fig. 8.

It was established that the flux through the membrane, or rate of transport with respect to Zn(II) was directly proportional to the concentration of Zn(II) in the external aqueous phase (Fig. 9) which was kept constant throughout the sampling period.

The passive sampler was calibrated for 4, 8 and 10 days of sampling and the corresponding calibration curves are shown in Fig. 10.

Design of a Flow-through Passive Sampler

A schematic diagram of another embodiment of the invention passive sampler is shown in Figs. 18 and 19, where a cell compartment is glued onto the original stainless steel washer (i.e. Part (f) of Fig. 11b was replaced by the component shown in Fig. 19 (Left).

Also, a schematic diagram of a flow-through passive sampling system, which incorporates the flow-through passive sampler, is shown in Fig. 20.

Flow-through Passive Sampler Experiments

A flow-through passive sampling system was set up according to Fig. 20, where the source was a bottle of solution containing zinc(II), which was connected to the passive sampler, and waste through tubes and a peristaltic pump, forming a single-pass sampling system. The PIMs used were composed of 40 % D2EHPA/ 60 % PVC, and the receiving phase

- 23 -

consisted of 0.1 M HNO_3 . The pump was set at a low flow rate of 0.16 mL min^{-1} . Samples of the receiving solution were taken at pre-determined periods of time (with replacement of fresh solution) and analysed for zinc(II).

- 5 For temperature experiments, the source bottle containing a solution of zinc(II) was placed in a thermostated water bath, and connected to an external water jacket containing the passive sampler. In the pH experiments, zinc(II) solutions were made up in 1.8 mM sodium nitrate for maintaining constant ionic strength and adjusted to the required pH using nitric acid or sodium hydroxide. These source solutions were replaced every 2 days
10 to prevent significant pH change due to the absorption of atmospheric carbon dioxide.

This proposed flow-through passive sampling system, unlike the “dip-in” system, allowed the maintaining of constant pH of the external bulk solution. This was achieved because the external bulk solution that had passed through the flow-through passive sampler was
15 discharged to the waste together with any acid that may have come across the membrane from the receiving phase. In addition, this approach allowed a constant concentration of the analyte at the external bulk solution/membrane interface. Experiments showed that although zinc(II) was extracted at a slower rate than in the case of the dip-in passive sampling system. This may be due to the much lower flow rate of liquid along the
20 membrane as compared to the flow rate generated by the underwater fish tank pump in the dip-in passive sampling experiments, which resulted in a smaller total amount of zinc(II) being exposed to the membrane.

2. Passive Sampling of NH_4^+

25 *Methodology/Objectives*

Development of a membrane-based passive ammonia sampler which can be applied to the detection of sewage contamination in stormwater drains over extended periods of time (days to weeks).

- 30 Polymer inclusion membranes (PIMs) to extract ammonia, using dinonylnaphthalenesulfonic acid (DNNSA) as the extractant, dodecanol as the plasticizer

- 24 -

and PVC as the base polymer were prepared. Some of the PIMs were prepared with purified or the original DNNSA (50 % m/m solution in heptane). Purification was conducted by evaporation of the heptane under vacuum to achieve the desired concentration of DNNSA.

5

PIMs preparation

The polymer (PVC), extractant (DNNSA) and plasticizer (dodecanol) were dissolved in tetrahydrofuran. The mixture was then poured into a glass ring and allowed to evaporate.

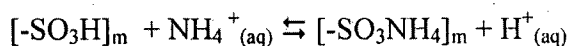
10 The composition of the PIMs studied is depicted in Table 3.

Table 3. Composition of PIMs studied.

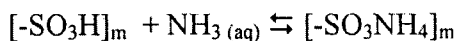
	A	B	C
Commercial DNNSA	40 ^a	30 ^b	
Purified DNNSA			16 ^c
Dodecanol		10	24
PVC	60	60	60

DNNSA concentrations (a) 0.4M; (b) and (c) 0.3M

15 When the membranes are used at $\text{pH} \leq 7$, the extraction process is ion-exchange involving the ammonium ion:



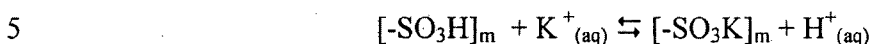
20 At higher pH ammonia is also present as NH_3 which can be extracted according to the following stoichiometric equation:



25 where subscripts m and aq refer to membrane and aqueous phase, respectively.

- 25 -

In order to mimic real conditions (constant pH), PIMs were first converted to the potassium form by immersing them in a 1 M KCl solution for about 24 h, according to the following equilibrium:



The choice of K^+ was based on the PIM selectivity: $\text{Na}^+ < \text{K}^+ < \text{NH}_4^+$

The $\text{NH}_4^+/\text{NH}_3$ passive sampler

- 10 A representation of the passive sampler device is shown in Figure 13 and an actual photograph of the device is shown in Figure 14. The receptacle comprises a receiver solution of 1 M KCl (10 mL). The PIM is held in place at the front end of the sampler and is exposed to both the receiver solution and the feed solution (aqueous system) which in this case is an ammonia source. The rear of the sampler is fitted with a sealable aperture
15 for adding or removing portions of the receiver solution before, during or after sampling.

Analysis

- A gas-diffusion flow injection system (GD-FIA) system with spectrophotometric detection was developed for the determination of ammonia in samples from the feed and receiver
20 solutions (Figure 15). The sample (200 μL) was injected into 2 M NaOH stream which was mixed with another 2 M NaOH stream to allow complete mixing of the sample with the 2 M NaOH solution. Under these conditions all ammonia (NH_3 and NH_4^+) was converted to NH_3 which diffused across the Teflon membrane of the gas-diffusion (GD) unit into the acceptor stream containing the acid-base indicators cresol red and thymol
25 blue. The colour change due change in pH caused by the diffusion of ammonia across the membrane was continuously monitored in the spectrophotometric flow-through cell as 580 nm.

The analytical figures of merit of the GD-FIA system include:

- 30 - concentration range: 0.70 – 6.0 $\text{mg L}^{-1}\text{NH}_4^+$
 - detection limit: 0.4 $\text{mg L}^{-1}\text{NH}_4^+$

- 26 -

reproducibility: less than 1.7% ($3.0 \text{ mg L}^{-1} \text{NH}_4^+$)

sampling frequency 30 hr^{-1} .

Glossary of Terms

2-NPOE	2-nitrophenyl octyl ether
BLMs	Bulk liquid membranes
CTA	Cellulose triacetate
CTB	Cellulose tributyrate
D2EHPA	Di(2-ethylhexyl) phosphoric acid
DBBP	Dibutyl butyl phosphonate
DC18C6	Dicyclohexano-18-crown-6
DNNSA	2,4-dinonylnaphthalene-1-sulfonic acid
DOP	Diethylphthalate
DOS	Diethylsebacate
ELMs	Emulsion liquid membranes
Kelex 100	7-(4-ethyl-1-methyloctyl)-8-hydroxyquinoline
LIX [®] 84-I	2-hydro-5-nonylacetophenone oxime
PIMs	Polymer inclusion membranes
PVC	Poly(vinyl chloride)
SLMs	Supported liquid membranes
T2EHP	Tris(2-ethylhexyl)phosphate
TBP	Tri-n-butyl phosphate
THF	Tetrahydrofuran
TOA	Tri-n-octyl amine
TODGA	N,N,N,N-tetraoctyl-3-oxapentanediamide
TOPO	Tri-n-octyl phosphine oxide

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THE CLAIMS:

1. A device for passive sampling of an aqueous system wherein the passive sampling device comprises a polymer inclusion membrane or a composite-polymer inclusion
5 membrane.

2. A device for passive sampling of an aqueous system comprising:
(i) a receptacle;
(ii) sampling aperture; and
10 (iii) a membrane which is a polymer inclusion membrane or a composite-polymer inclusion membrane;
wherein
(a) the receptacle contains a receiver solution and is fitted with the sampling aperture to allow for the addition or removal of the receiver
15 solution from said receptacle, and
(b) the membrane is in fluid communication with both the receiver solution and the aqueous system.

3. A device for passive sampling of an aqueous system, comprising:
20 a housing defining a cavity for a receiver solution, the cavity having an opening spanned by a membrane which is a polymer inclusion membrane or a composite-polymer inclusion membrane;
wherein the membrane includes an inner surface which is contactable with the receiver solution and an outer surface which is contactable with the aqueous system such
25 that the membrane is in fluid communication with both the receiver solution and the aqueous system.

4. A device for flow-through passive sampling of an aqueous system comprising:
(i) a receptacle containing a receiver solution;
30 (ii) a cell compartment containing the aqueous system;
(iii) a sampling aperture which is fitted to the receptacle to allow for the addition

- 28 -

or removal of the receiver solution from said receptacle,

wherein:

- 5 (a) the cell compartment is connected to the receptacle whereby the receiver solution and the aqueous system are separated by a membrane which is a polymer inclusion membrane (PIM) or a composite-PIM being in fluid communication with the receiver solution by its inner surface and also the aqueous system by its outer surface, and
- 10 (b) the cell compartment comprises an inlet and outlet to allow a flow of liquid from the aqueous system to contact the outer surface of the PIM or composite-PIM.

5. A process for passive sampling of an aqueous system including the step of immersing a passive sampling device into said aqueous system wherein the passive sampling device comprises a polymer inclusion membrane or a composite-polymer inclusion membrane.

15

6. A process for passive sampling of an aqueous system including the step of transferring a flow of water through a passive sampling device wherein the passive sampling device comprises a polymer inclusion membrane (PIM) or a composite-polymer inclusive membrane and whereby the flow of water comes into contact with the PIM or composite-PIM.

20

7. A process according to claim 5 or claim 6 wherein the passive sampling device is as defined in any one of claims 1 to 4.

25

8. A device or process according to any one of claims 1 to 7 wherein the PIM comprises from about 40 to 80% (m/m) of a polymer based on the total PIM composition.

9. A device or process according to any one of claims 1 to 8 wherein the PIM comprises from about 5 to 40% (m/m) of an extractant based on the total PIM composition.

30

- 29 -

10. A device or process according to any one of claims 1 to 9 wherein the PIM comprises from about 0 to 30% (m/m) of a plasticizer/modifier based on the total PIM composition.
- 5 11. A device or process according to claim 8 wherein the polymer is PVC.
12. A device or process according to claim 9 wherein the extractant is a sulphonic acid or a salt thereof, preferably DNNSA or a salt thereof.
- 10 13. A device or process according to claim 9 wherein the extractant is an alkyl phosphoric acid, preferably D2EHPA or D2EHDTPA.
14. A device or process according to claim 13 wherein the extractant is D2EHPA.
- 15 15. A device or process according to claim 9 wherein the extractant is a quaternary amine, preferably Aliquat 336.
16. A device or process according to any one of claims 1 to 6 for the passive sampling of ammonia wherein the PIM comprises about 50 to 70% (m/m) of PVC; and about 10 to
20 30% (m/m) of DNNSA (or a salt thereof) based on the total PIM composition.
17. A device or process according to any one of claims 1 to 6 for the passive sampling of zinc(II) wherein the PIM comprises about 50 to 70% (m/m) of PVC, and about 30 to 50% (m/m) of D2EHPA based on the total PIM composition.
- 25 18. A device or process according to any one of claims 1 to 17 wherein the PIM is composite PIM wherein a non-PIM polymer layer is attached to the PIM.
19. A device or process according to claim 18 wherein the non-PIM polymer layer is
30 Nafion® or a microporous membrane layer.

- 30 -

20. A device or process according to claim 18 or claim 19 wherein the non-PIM polymer layer is exposed to the aqueous system.

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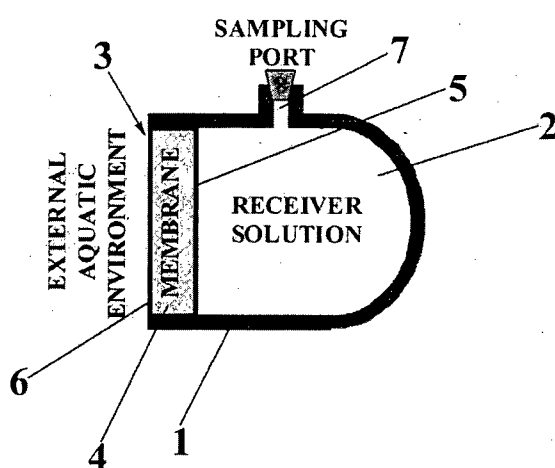
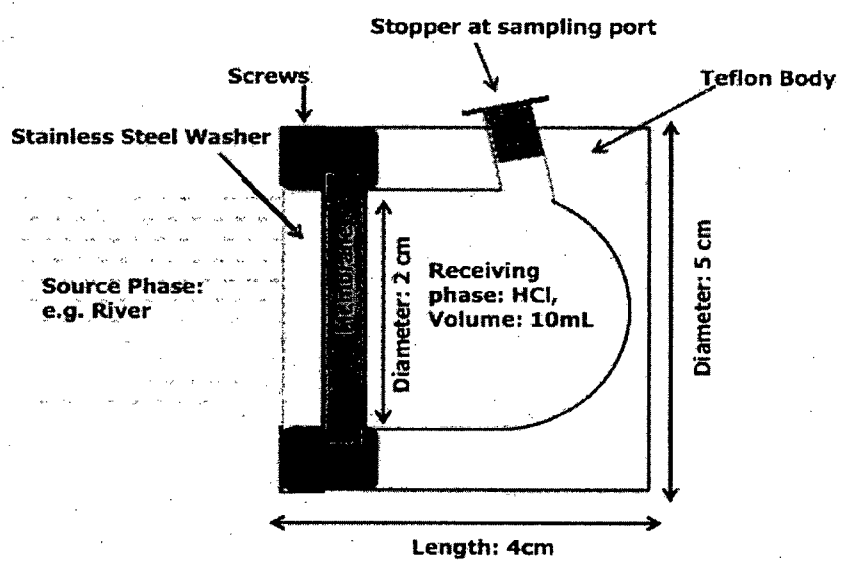
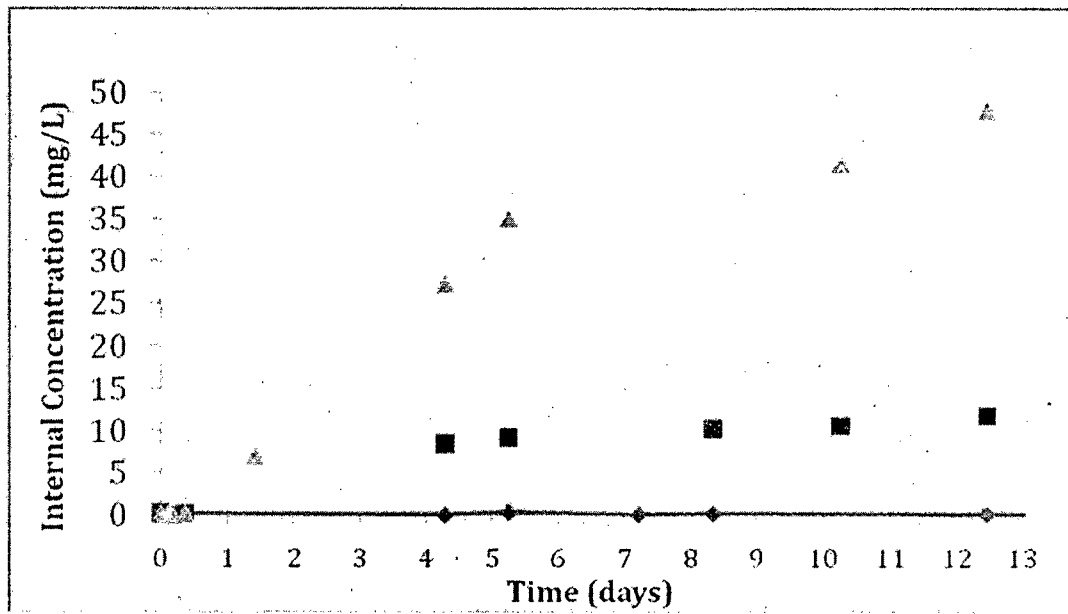


FIGURE 1

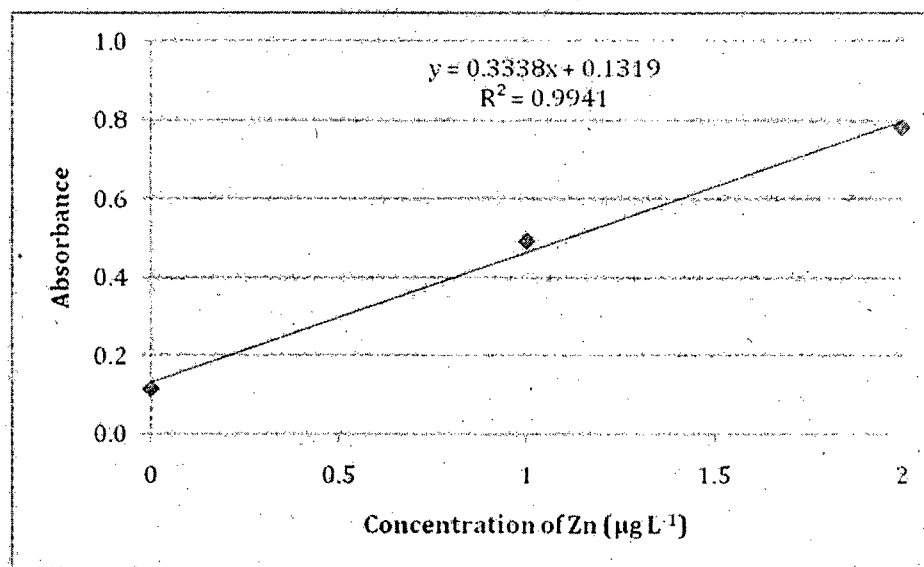
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**FIGURE 2**

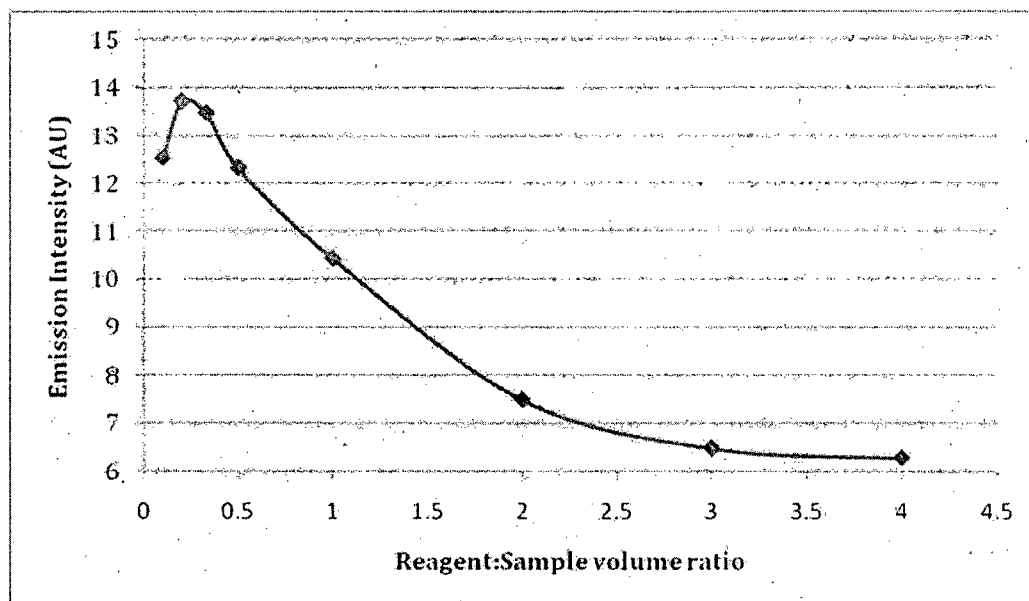
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**FIGURE 3**

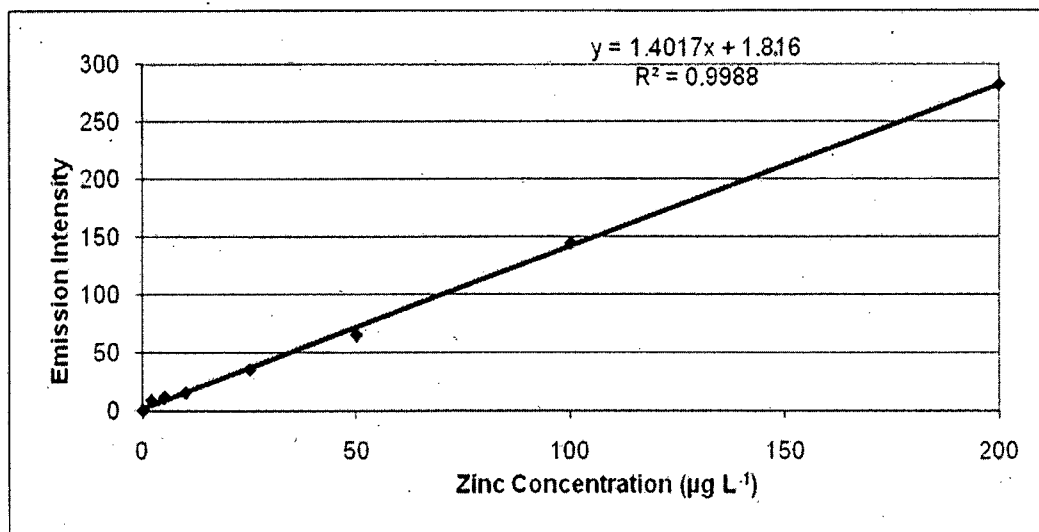
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**FIGURE 4**

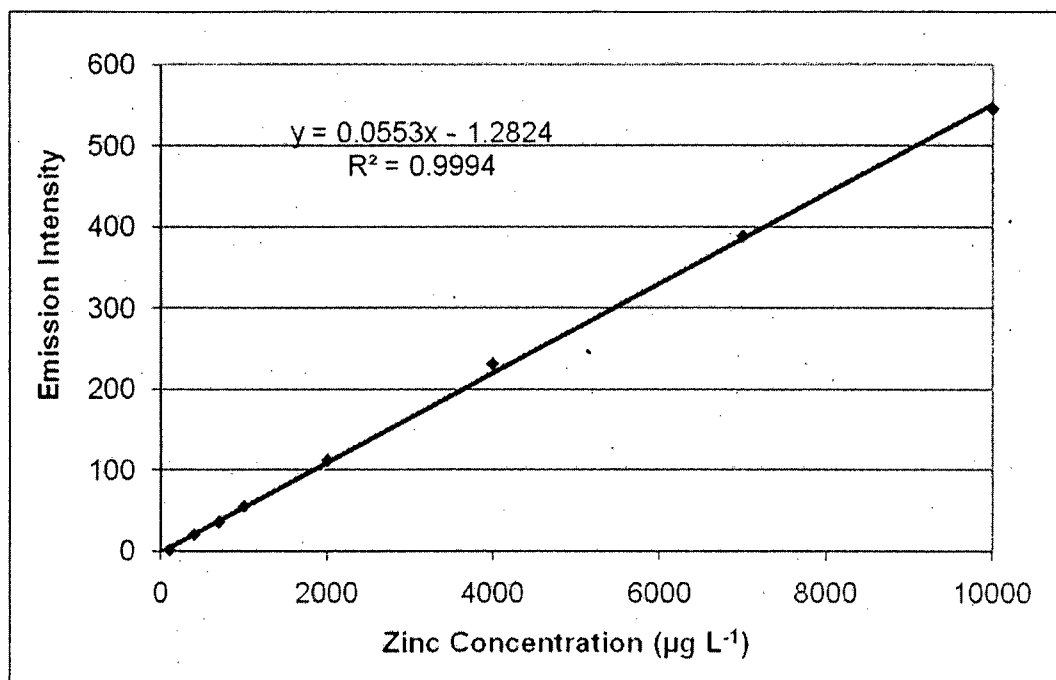
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**FIGURE 5**

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**FIGURE 6**

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**FIGURE 7**

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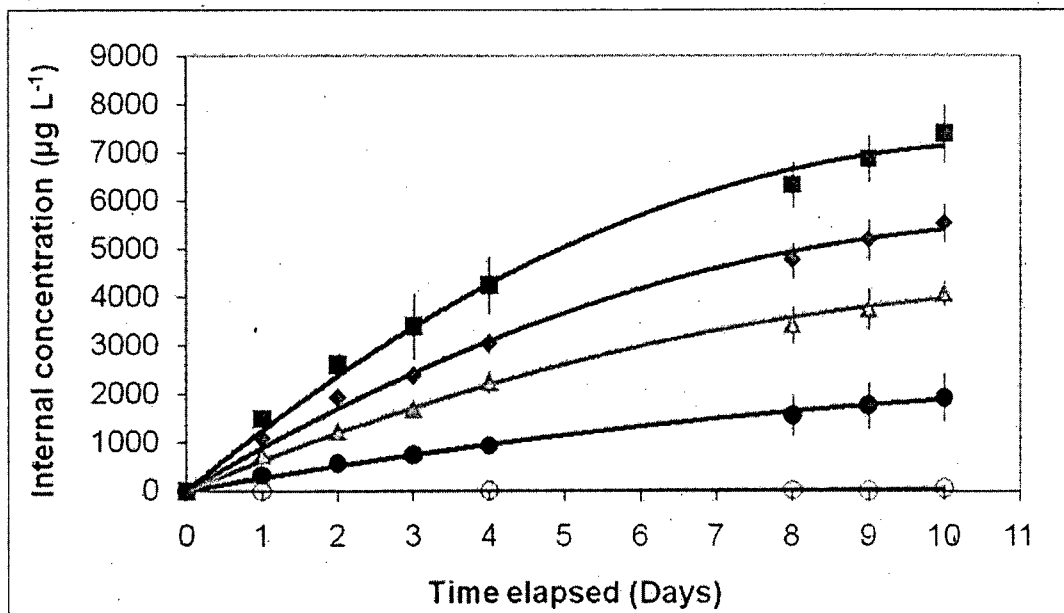


FIGURE 8

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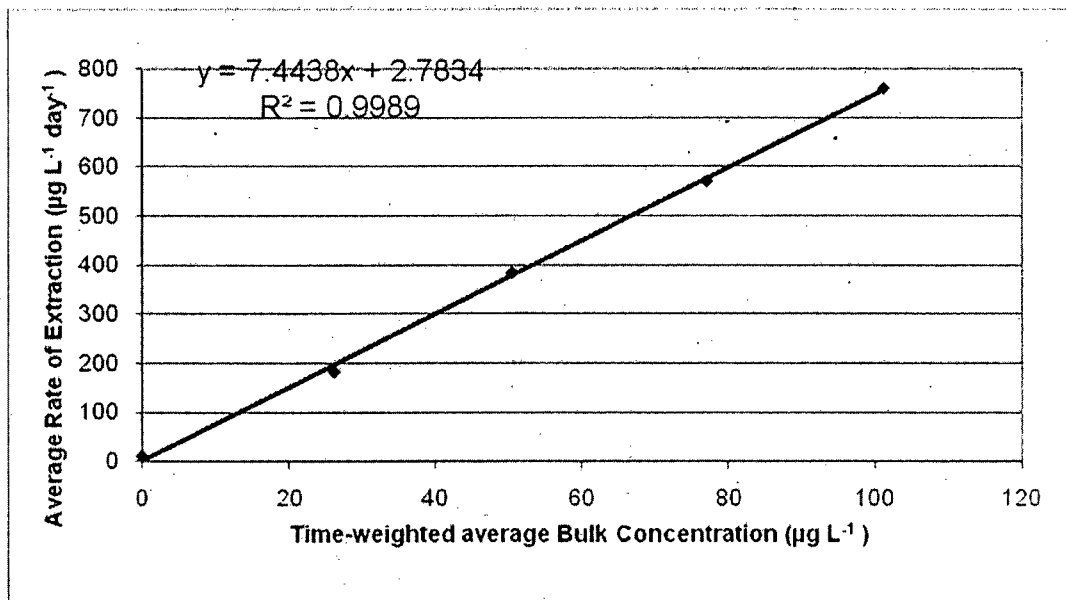
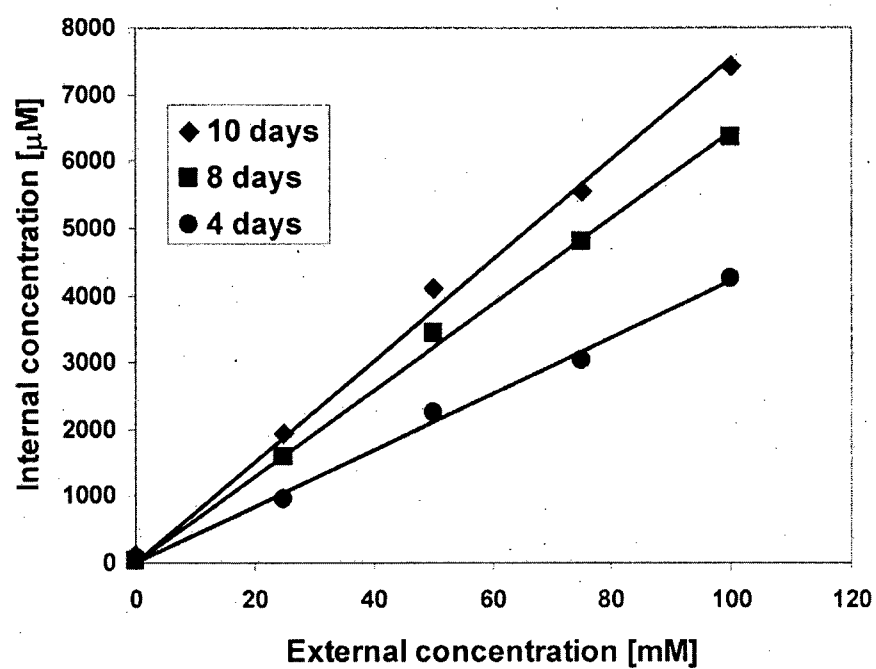


FIGURE 9

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**FIGURE 10**

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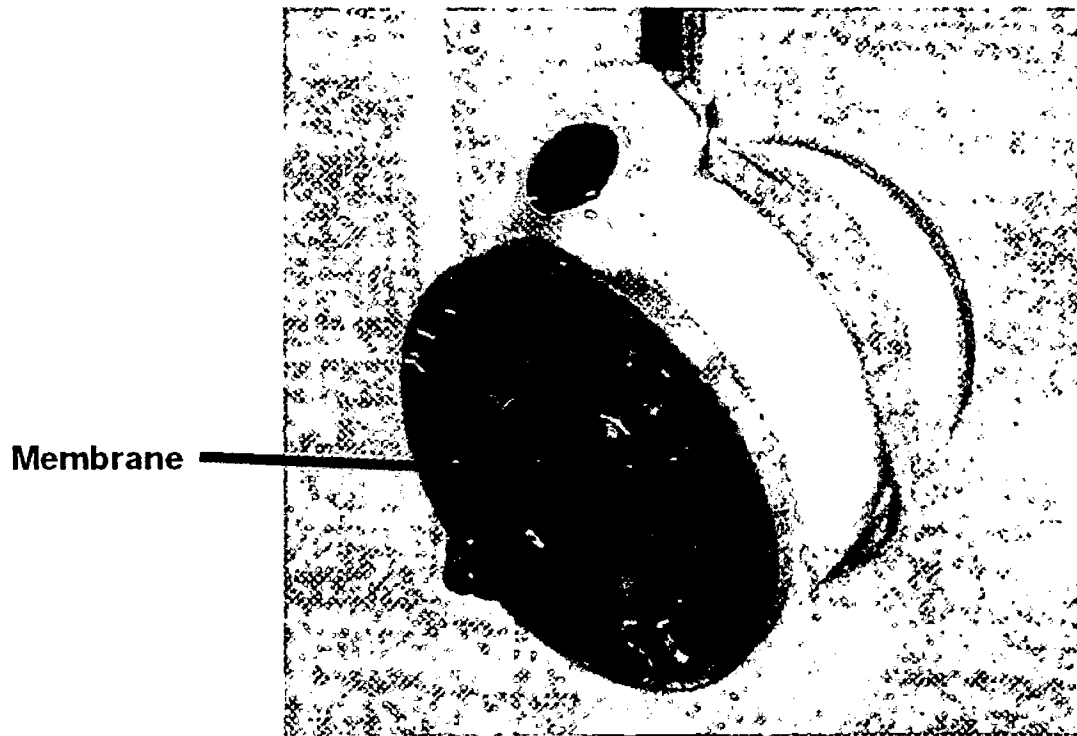


FIGURE 11a

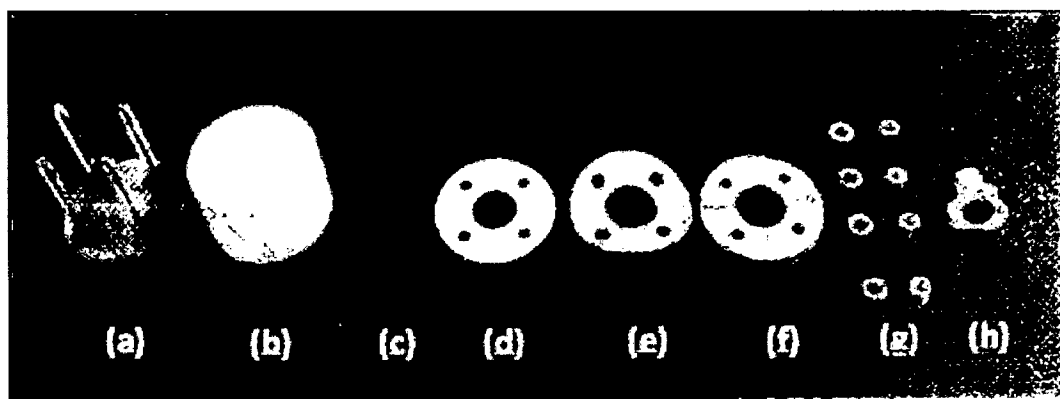
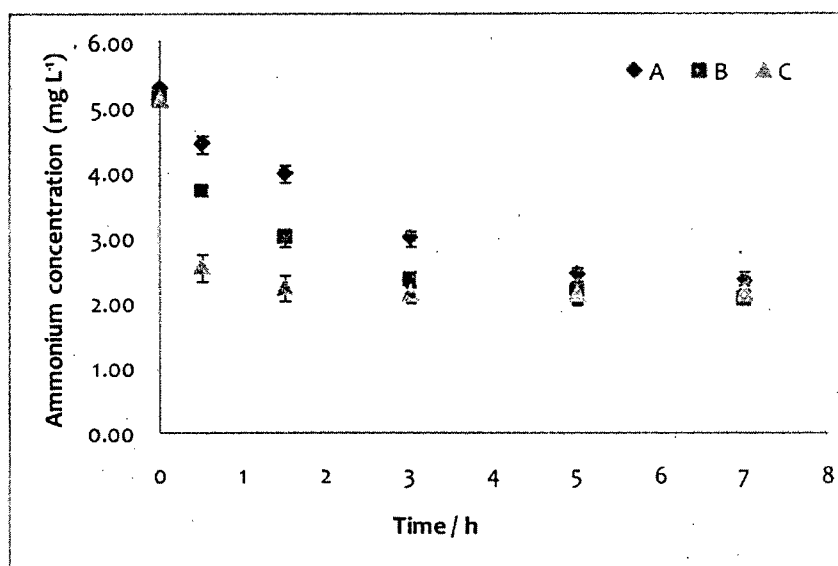


FIGURE 11b

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**FIGURE 12**

- 13 / 20 -

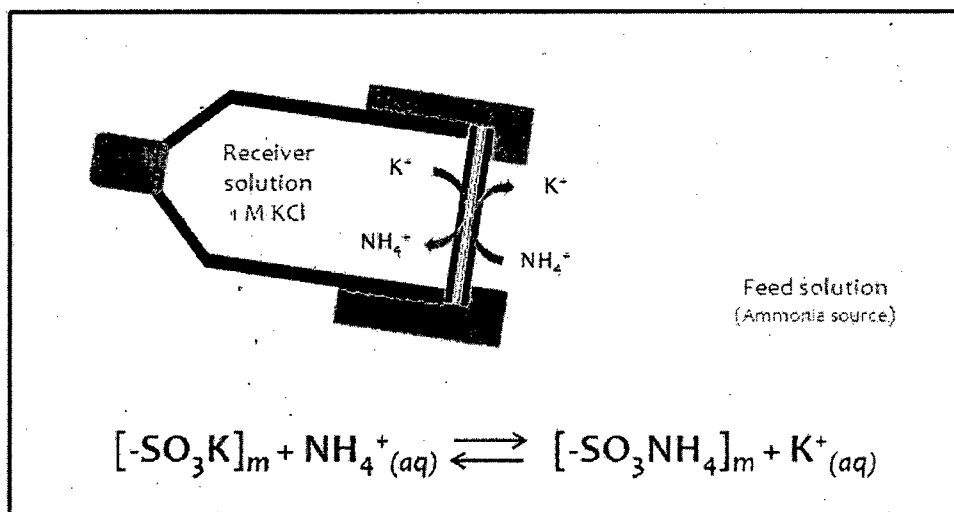


FIGURE 13

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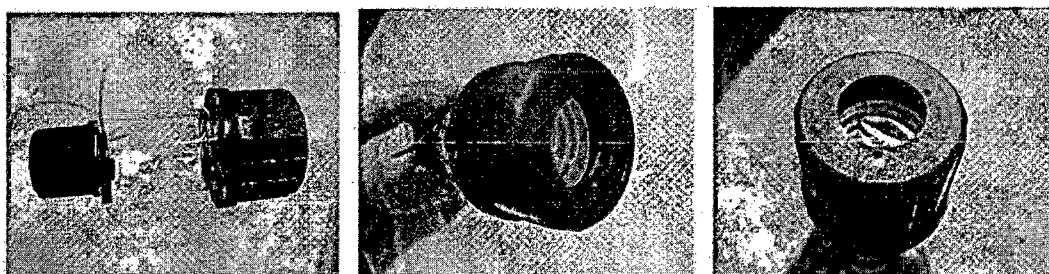
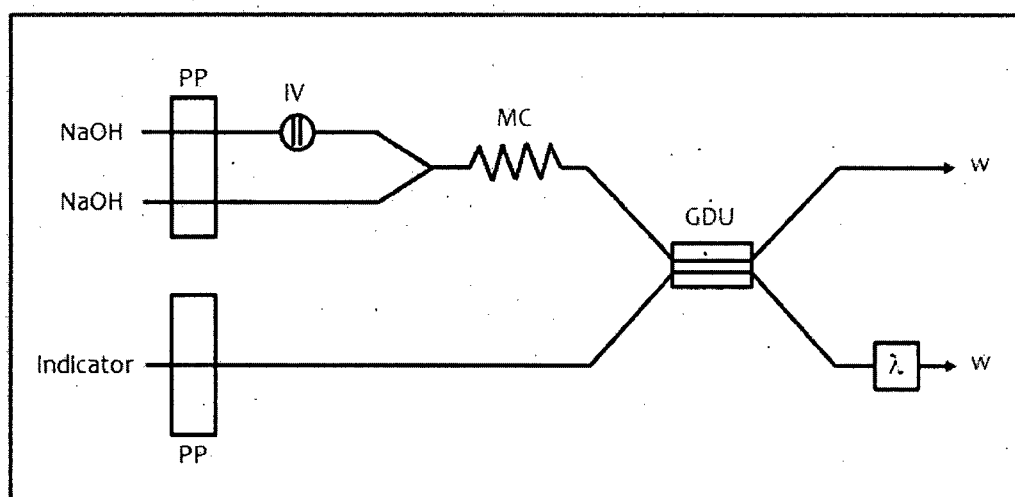
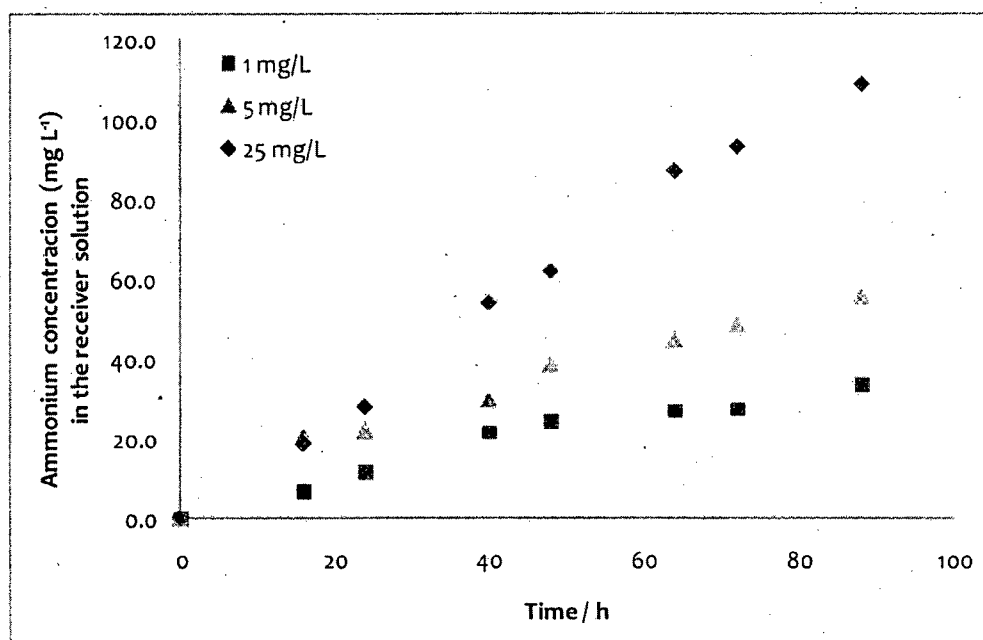


FIGURE 14

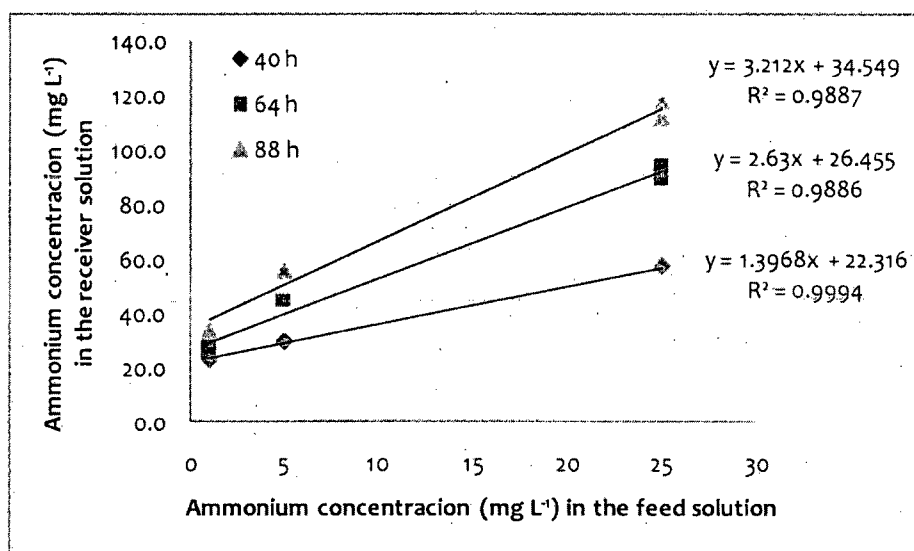
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**FIGURE 15**

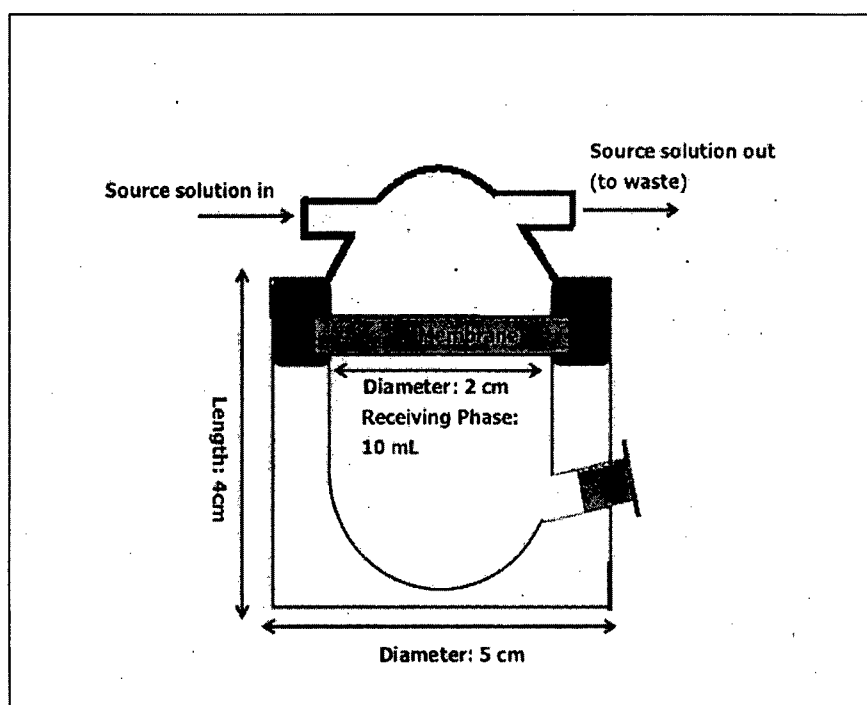
- 16 / 20 -

**FIGURE 16**

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**FIGURE 17**

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**FIGURE 18**

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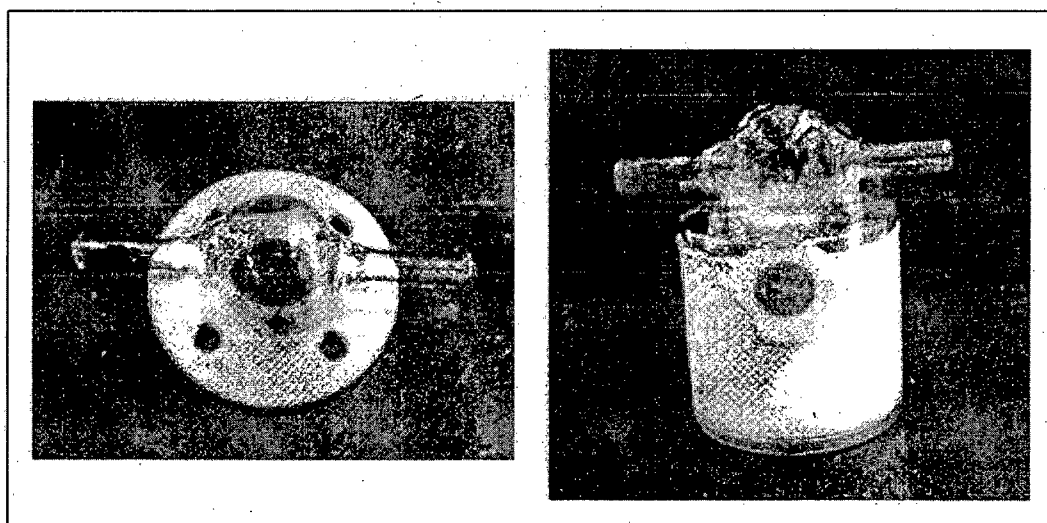
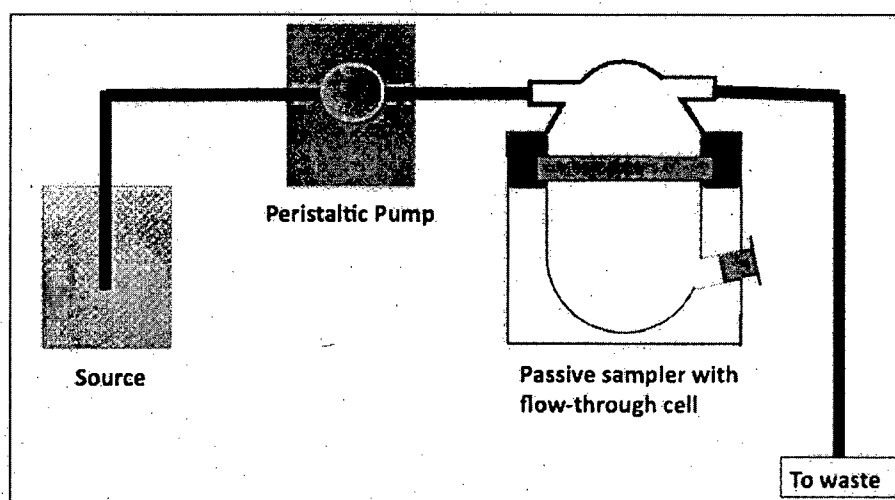


FIGURE 19

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**FIGURE 20**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2011/001571

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

G01N 33/18 (2006.01)

G01N 1/10 (2006.01)

B01D 71/28 (2006.01)

B01D 71/16 (2006.01)

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)

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)

- 1) EPODOC & WPI: IPC & ECLA G01N 1/10 - 1/20, G01N 33/18, B01D 61/-, B01D 63/-, B01D 65/- and KEYWORDS sampling, measure, monitor, membrane, polymer inclusion, ion exchange, water, aqueous, and similar terms.
- 2) EPODOC & WPI: KEYWORDS polymer inclusion, polymer liquid, gelled liquid, polymeric plasticised, fixed site carrier, solvent polymeric, membrane, sampling, measure, monitor, water, aqueous, and similar terms.
- 3) US, WO, GB, EP, AU English language full-text: IPC G01N 33/18, G01N 1/-, and KEYWORDS polymer inclusion, polymer liquid, gelled liquid, polymeric plasticised, fixed site carrier, solvent polymeric, membrane, sampling, measure, monitor, water, aqueous, and similar terms.
- 4) INSPEC: polymer inclusion, polymer liquid, gelled liquid, polymeric plasticised, fixed site carrier, solvent polymeric, membrane, sampling, measure, monitor, water, aqueous, ammonia, and similar terms.
- 5) EPODOC & WPI: IPC & ECLA B01D 71/- and KEYWORDS PVC, DNNSA, ammonia, and similar terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KOLEV, S D et al., 'Solid phase extraction of zinc (II) using PVC-based polymer inclusion membrane with di(2-ethylhexyl)phosphoric acid (D2EHPA) as the carrier', Talanta Volume 78, Issue 3, 15 May 2009, pages 795 - 799 Whole document	1 - 9, 11 - 14, 16 - 20
Y	US 4092117 A (BYRNE) 30 May 1978 column 16 line 3 - 15, column 28 line 61 - column 31 line 40, and figures 8, 17 and 18	1 - 20



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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search
09 February 2012Date of mailing of the international search report
27 February 2012

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2011/001571

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KEBICHE-SENHADJI, O et al., 'Facilitated Cd(II) transport across CTA polymer inclusion membrane using anion (Aliquat 336) and cation (D2EHPA) metal carriers', Journal of Membrane Science Volume 310, Issues 1-2, 5 March 2008, Pages 438-445 Whole document	1 - 10, 15, 18 - 20
Y	NAZARENKO, A Y et al., 'Selective Transport of Lead(II) and Strontium(II) Through a Crown Ether-Based Polymer Inclusion Membrane Containing Dialkyl-naphthalenesulfonic Acid', Journal of Inclusion Phenomena and Macrocyclic Chemistry, Volume 29, 1997, Pages 247-258 Page 249	12, 16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2011/001571

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member	
US	4092117	GB	1556050
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.			
END OF ANNEX			