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A separation and preconcentration process for metal speciation using a liquid membrane: A case study for iron speciation in seawater

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ABSTRACT

An efficient assisted transport of Fe(III) ions using a bulk liquid membrane containing 2-hydroxybenzaldeyde benzoylhydrazone in toluene has been applied as a separation and preconcentration process for the analysis and speciation of dissolved iron traces in natural and sea waters. A study strategy based on a modified simplex design has been followed to optimise the transport of Fe(III) ions through the liquid membrane. Maximum carrier-mediated transport efficiencies were obtained at following conditions: pH 1.9 for feed aqueous solution; 0.014 mol L^{-1} of ligand in toluene as carrier and 2.9 mol L^{-1} HNO_3 in the stripping solution. Under optimal conditions, the average recovery of Fe(III) ions was 102 ± 2% (n = 7) for 6 h at 35 °C and the preconcentration factor of the method was 18.1. The influence of saline matrix was negligible and experiments at slightly high temperatures led to reduced preconcentration times. The accuracy of the method was verified by using the TMDA-62 certified reference water sample and successfully applied to the analysis of Fe(III) in river and seawater samples from Tangier (Morocco). Due to the proposed liquid membrane system allowed the selective separation and preconcentration of Fe(III) ions but not Fe(II) ions, a scheme for speciation analysis of dissolved iron was proposed. The distribution of total dissolved Fe, non-labile Fe, labile Fe(II) and labile Fe(III) fractions was performed in real seawater samples with successful results in good agreement with those obtained by adsorptive cathodic stripping voltammetry (average relative error of ± 3%).

1. Introduction

Iron is an essential element for the biochemical and physiological functioning of terrestrial and oceanic organism including phytoplankton, acting as a limiting factor regulating primary production in high-nutrient low-chlorophyll regions (Boyd and Ellwood, 2010; Thuróczy et al., 2011). The analysis and speciation of iron in aquatic systems is very important for environmental and biological studies, because its chemical forms influence not only the bioavailability of iron, but also the physico-chemical and toxicological properties of other trace elements and organic substances (Lin and Twining, 2012). Iron speciation in natural waters mainly deals with the different physico-chemical forms of the most common oxidation states of iron: Fe(II) and Fe(III) (Chen et al., 2015). They include different fractions of particulate, colloidal and dissolved metal, existing as charged and neutral inorganic ions (i.e. for Fe(II), it is primarily Fe^{2+}, $FeCl^{+}$, $FeSO_4$, $FeCO_3$ and $FeOH^{+}$; while for Fe(III), different hydroxide species, such as $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe(OH)_3$ are predominant with only partial contribution of Fe^{3+}), and diverse organic complexes of Fe(II) and Fe (III) of different lability, as well as operationally defined fractions (vanLoon and Duffy, 2011; Calza et al., 2012; Rivaro et al., 2012).

In water, Fe(II) is a soluble species but it is rapidly oxidised in oxygen rich environments; Fe(III) is thermodynamically stable but with a low solubility (Achterberg et al., 2001; Lin and Twining, 2012). Thus, iron is present in very low levels in seawater with dissolved concentrations below 1 nmol L^{-1} (Millero, 2013), being in many areas of the surface ocean near 20–30 pmol L^{-1}; in estuaries and coastal water, dissolved iron concentrations can vary from 1 to 10 nmol L^{-1} but higher levels can be found in heavily polluted areas (Laglera and van den Berg, 2009; Roy and Wells, 2011); the iron concentration in freshwater can be higher ranging over 0.05–3 μmol L^{-1} (Nagai et al., 2007). The presence of organic compounds increases the overall solubility of iron, being up to 99% of total iron complexed to organic ligands in marine environments (Roy and Wells, 2011; Lin and Twining, 2012).

The determination of total dissolved iron and iron speciation in seawater requires rigorous analytical methods in order to provide high quality data that will improve our understanding of its biogeochemical

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cycling and the interaction between iron species and phytoplankton growth. The low concentrations of iron species in water require analytical techniques with appropriate detection limits. A variety of well-established methods for quantitative analysis of iron have been developed, standing out atomic spectroscopy methods because they are widely employed and seem a good choice because of their simplicity, high sensitivity and quickness (Chen et al., 2012).

Due to the natural low concentration of iron in water, separation or preconcentration before analysis usually becomes necessary (Shamspur and Mashhadizadeh, 2005; Jamali et al., 2016), especially in the analysis of seawater samples, since the saline matrix may produce considerable interferences (Jerez Veguería et al., 2013). Liquid membrane methodology (LM) is a novel alternative for sample pretreatment which combines solvent extraction and stripping process in a single step (Cox, 2008; Ramkumar and Chandramouleeswaran, 2015; Diaconu et al., 2016). The liquid membrane is a liquid phase separating two immiscible solutions (feed and stripping phases, usually aqueous solutions). Transport of chemical species across LM occurs because of diffusivity and solubility differences between the aqueous phases and the membrane. However, dissolving a carrier into the LM may enhance solute flux across it (Rounaghi et al., 2016). The carrier acts as an extractant agent favoring analyte transport from the feed solution to the stripping solution, due to its ability to complex with the analyte (facilitated transport) (López-López et al., 2010). When applied to the metal ions preconcentration, carrier-mediated transport across LM usually takes place as facilitated coupled counter transport, where the metal ions are exchanged with H^+ ions facilitated by acidic carriers (Zoubi et al., 2014). This system enables the separation and preconcentration of metal ions from complex matrices and the stripping solution containing the separated metal ions is very suitable for atomic spectroscopic analysis (Kislik, 2010). When the used carrier is selective for a specific metal species, methodologies for speciation analysis can be developed (Mirea et al., 2016). Among the different liquid membrane configurations, bulk liquid membranes (BLMs) are suitable for screening a novel carrier-mediated transport system on the laboratory scale and are appropriate for application as analytical tools, because of the simplicity, reducing operation costs and easy accessibility of the aqueous phase (Ramkumar and Chandramouleeswaran, 2015; Diaconu et al., 2016).

The application of LMs in environmental analysis is still very recent. The earliest works appeared < 20 years ago and comprised separation and preconcentration of heavy metals in river and lake waters with few applications to seawater analysis (Granado-Castro et al., 2008; Domínguez-Lledó et al., 2007; Aouarram et al., 2007; Falaki et al., 2016; Zahedi and Ghasemi, 2016) and metal speciation (López-López et al., 2010; Parthasarathy et al., 2010).

In this paper a bulk liquid membrane system has been developed and applied to the separation and preconcentration of dissolved iron traces, which enables its speciation analysis in water. A liquid membrane containing 2-hydroxybenzaldehyde benzoylhydrazone (2-HBBH; also called salicylidene benzoylhydrazone) as chelating carrier has been proposed allowing the selective transport of Fe(III) and the design of a speciation scheme for Fe(II) and Fe(III) ions. 2-HBBH acts as tridentate chelating agent with outstanding biological relevance to both copper and iron complexes. This hydrazone has also great interest on analytical applications having been used as chromophore and fluorescence chemosensor as well as in adsorptive cathodic stripping voltammetry (Espada-Bellido et al., 2009), but until now it has not been applied as carrier in a liquid membrane system.

2. Experimental

2.1. Apparatus

The bulk liquid membrane studies were carried out using a homemade quartz device, which consisted of two concentric beakers (a cylindrical cell of 11.3 cm i.d. and 5.4 cm height with a concentric tube of 2.6 cm i.d. and 3.0 cm height; described elsewhere (Aouarram et al., 2007). The feed solution (V_f = 260 mL) was placed into the external cylinder while the stripping solution (V_s = 12 mL) was placed into the internal cylinder. The organic solution used as liquid membrane was placed over both aqueous solutions using a volume of 70 mL. Both aqueous solutions in the cell were stirred with two Teflon-coated magnetic bars (12 × 4 mm), by using a model Agimatic-S magnetic Stirrer (Selecta, Spain). Organic liquid membrane containing the transport agent was added over the feed and the stripping solutions with an effective membrane interface of 95.8 cm^2. In these conditions the preconcentration factor of the cell (PF) was 21.7 calculated by the ratio V_f/V_s. The temperature of experiments was controlled by using a Tectron-Bio thermostatic bath (Selecta, Spain).

The pH measurements were made with 2001 pH Meter using a 52–02 combined glass-Ag/AgCl electrode (Crison, Spain). Organic matter was removed from real water samples by UV irradiation with a Metrohm model 705 UV Digester (Metrohm, Switzerland) in quartz tubes.

Metal concentration measurements in acid solutions were performed using a Solaar M Series atomic absorption spectrophotometer (Unicam, United Kingdom) with flame (FAAS) or graphite furnace (GFAAS) atomization systems and following the instrumental conditions recommended by the manufacturer. Pyrolytic coated graphite tubes and Zeeman background corrector were used for GFAAS analysis (for blanks measurements and very low iron concentrations) and air-acetylene flame and deuterium background corrector for FAAS determinations. Voltammetric measurements in saline samples were carried out by using a Metrohm model 757 VA Trace Analyser processor with a Metrohm 747 VA electrode stand (Metrohm, Switzerland) and an automated hanging mercury drop electrode (HMDE) as working electrode. For UV–Vis spectroscopic measurements, a Unicam Helios Gamma & Delta (Unicam, United Kingdom) spectrophotometer with 1.00 cm quartz glass cells (1.00 cm × 1.00 cm × 4.5 cm) was used.

Sample handling and preparation of solutions were performed under a class 100 laminar flow hood cabinet Crusair model 9005-FL (Cruma, Spain). Water was ultrapurified by reverse osmosis with an Elix 3 (Milli-RO) system followed by ion exchange with an 18 MΩ cm deionised Milli-Q50 system (Millipore, USA).

Water samples were collected using a peristaltic pump (Masterflex 7521-00, poppet head 07518–10, Cole-Parmer Instrument Co. Illinois USA), rigid Teflon pipes (FEP A-06450-07) and Tygon flexible tubing (6424–71). They were filtered using a 0.45 μm Calyx Capsule MSI filter (3/8″ barb, 1/PK, polypropylene; Osmonics, USA) connected on line with the Tygon tubes.

2.2. Reagents and solutions

All reagents and solvents were of the highest purity available (pro analysis or Suprapur grades). Aqueous solutions of Fe(III) were prepared using an iron standard solution of 1000 mg L^{-1} (Merck, Darmstadt, Germany) in 0.05 mol L^{-1} HNO_3. A stock solution of 0.7 g L^{-1} Fe(II) was prepared by dissolving $(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$ in 0.01 mol L^{-1} HCl and purged with high purity nitrogen (Praxair, Spain) for 5 min. Chloroacetate buffer (4 mol L^{-1}) was prepared by adding potassium hydroxide to chloroacetic acid solution and it was used to adjust the pH of feed solutions (pH 1.5–3.5). The salts, acid and basic reagents were purchased from Merck (Darmstadt, Germany).

The following compounds were used as complexing agents for Fe(II) ions: 0.9×10^{-3} mol L^{-1} of 2,2′-Bipyridyl (Bp) (ReagentPlus®, ≥ 99%) dissolved in 0.01 mol L^{-1} HCl; and aqueous solution of 0.06×10^{-3} mol L^{-1} 1,10-phenanthroline (≥ 99%). Also, the following reducing agents were used to avoid the oxidation of Fe(II) to Fe (III): sodium thiosulphate pentahydrate (ACS reagent, 99.5%); sodium pyrophosphate tetrabasic (reagent grade, ≥ 95%) and L-ascorbic acid (reagent grade). Aqueous solutions of 10^{-3} mol L^{-1} of these reagents