



ELSEVIER

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of labile barium in petroleum-produced formation water using paper-based DGT samplers

Wellington de Oliveira^{a,b}, Maria de Fátima Batista de Carvalho^c, Eduardo de Almeida^d, Amauri Antonio Menegário^b, Roberto Naves Domingos^b, Ana Luiza Brossi-Garcia^b, Virgílio Franco do Nascimento Filho^d, Ricardo Erthal Santelli^{e,*}

^a Programa de Pós-Graduação em Geociências e Meio Ambiente, Instituto de Geociências e Ciências Exatas, UNESP - Univ Estadual Paulista, Av. 24-A, 1515, CEP 13506-900, Rio Claro, SP, Brazil

^b Centro de Estudos Ambientais, UNESP - Univ Estadual Paulista, Av. 24-A, 1515, CEP 13506-900, Rio Claro, SP, Brazil

^c PETROBRAS/CENPES/PDP/Célula de Tratamento e Reuso de Água, Av. Horácio Macedo 950, Cidade Universitária, Rio de Janeiro, RJ, Brazil

^d Centro de Energia Nuclear na Agricultura, Universidade de São Paulo, Av. Centenário 303, 13416-000, Piracicaba, SP, Brazil

^e Universidade Federal do Rio de Janeiro, Departamento de Química Analítica, Av. Athos da Silveira Ramos 149, Bloco A, Cidade Universitária, 21941-909 Rio de Janeiro/RJ, Brazil

ARTICLE INFO

Article history:

Received 12 May 2012

Received in revised form

9 August 2012

Accepted 9 August 2012

Available online 18 August 2012

Keywords:

Produced formation water

DGT

Barium

P81 membrane

Fractionation

Speciation

ABSTRACT

A polyacrylamide hydrogel containing the Chelex-100 resin has traditionally been used as the binding agent for the diffusion gradients in thin films (DGT) technique. The Chelex-100 resin, although important for the determination of various transition metals, is unsatisfactory for the determination of alkaline earth metals, particularly Ba. In this paper, a cellulose membrane, treated with phosphate (P81 membrane), was evaluated as a binding agent for DGT devices for the determination of Ba in produced formation water (PFW) samples. In addition, diffusive layers of filter paper (cellulose) were tested to diffuse Ba through the DGT devices. Experiments to evaluate the key variables of the technique (pH, deployment time, and ionic strength/salinity) were performed. The Ba sampled by these DGT devices was measured using inductively coupled plasma optical emission spectrometry. Aiming to generate information (related to bioavailability of Ba) on the reuse of PFW for irrigation, the determination of Ba in onshore and offshore samples was performed. The new approach was effective for determination of Ba in onshore samples. To determine Ba in offshore samples, it was necessary to use an alternative calibration procedure due to the high NaCl concentration in these samples.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Produced formation water (PFW) is usually a mixture of the water naturally present in the geological formation of the oil reservoir and the injected water used to increase the oil production. PFW is potentially dangerous to the environment mainly due to the large volume that is produced, that can be 10 times the volume of the hydrocarbon produced. For example, during 1990, Gulf Mexico oilfield operation resulted in about 900,000,000 barrels of waster [1]. The environmental risks associated with PFW may change depending on the characteristics of the location where it occurs, its distribution and its final chemical composition. The PFW components originate from the reservoir, injected seawater and chemicals used in oil production. Specifically, these components generally include the following: minerals, dissolved

gases, dissolved (and dispersed) oily constituents (generated during the producer formation), corrosion inhibitors, demulsifiers, biocides and kidnapping H₂S (chemicals used during the production process) [2].

When the water used for irrigation contains a high concentration of Ba, a toxic effect on plant life can occur that inhibits the photosynthetic rate by inducing stomatal closure and difficulty in carbon fixation [3,4]. For example, 5 mmol L⁻¹ Ba treatment induced stomatal closure and perturbed carbon-fixation-related metabolism in soybean [3]. It is noteworthy that the soluble form of Ba can be accumulated by plants, which can result in toxicity for other organisms because the Ba accumulation can be transferred to animals [5].

Determining the total Ba content in PFW does not provide all the necessary information to make appropriate reuse of this effluent, for example in agriculture. Recent studies show the importance of conducting measurements of the labile fraction of metals because this fraction is considered to be potentially bioavailable [6–10]. Therefore, in addition to the concentration, the chemical forms in which the Ba exist in the PFW can

* Corresponding author. Tel.: +55 2125627892; fax: +55 21 26292234.
E-mail addresses: santelli@iq.ufirj.br, santelli@geoq.uff.br (R.E. Santelli).

significantly affect its availability to plants and, consequently, to animals. Thus, it is extremely important to evaluate the labile fraction of Ba in PFW.

DGT is a promising tool for fractionating the labile portion of the solubilized metals present in aqueous system [11,12]. Conventional DGT design allows for the determination of free ionic metals and complex inorganic and organic compounds containing low molecular weight metals, excluding large particles and colloids (which are not quantified). Only complexes that dissociate into smaller time-scale of minutes can be measured. This includes complexes with fulvic acid and metals, but excludes complexes with strong ligands [13]. Another advantage of DGT is that it provides the mean (by time) concentration values in the aqueous system instead of the concentration only at the time of collection [11,12]. This characteristic can be useful, for example, to use DGT to measure Ba directly in plant for treatment of produced water.

The DGT device uses a diffusion agent, conventionally a polyacrylamide hydrogel and a binding agent, which is typically Chelex-100 resin supported on a polyacrylamide hydrogel. The function of the diffusion agent is to promote diffusion of the metallic element, for ultimate capture by the binding agent, that is independent of changes in the flow system where the device is immersed. The binding agent must retain the element for its concentration to be determined quantitatively. DGT devices assembled using the Chelex-100 resin are unsatisfactory for the determination of alkaline earth metals, particularly Ba [14].

Some alternative materials have been evaluated as binding phases for DGT devices [15]. The AG50W-X8 cation-exchange resin has been used in DGT samplers for the measurement of Cs and Sr [16]. Copper ferrocyanide (CFCN) immobilized on Chelex-100 resin gels (Chelex-CFCN) and on poly(acrylic acid) gels (PAA-CFCN) were successfully applied for the measurement of low levels of stable ^{133}Cs and radioactive ^{137}Cs in synthetic solutions and in natural river waters [17].

Cellulose phosphate ionic exchange (Whatman P81 membrane) [18] has been successfully used for the retention of Cu^{2+} , Ca^{2+} , Zn^{2+} , Mn^{2+} , Ni^{2+} , K^+ , Na^+ , Ca^{2+} and Mg^{2+} from a synthetic sample. The membrane is potentially useful as a cationic exchanger for analysis of other alkaline earth metals such as Ba.

Cellulose membrane (commercially available as 3 MM chromatographic paper) was proposed [19] as an alternative diffusive material. Compared to conventional materials, cellulose membranes present some problems to be used in DGT devices: water contents and pore size frequently vary and, consequently, measurements of diffusion coefficients must be rigorously controlled. The primary advantages of 3 MM chromatographic paper are the increased resilience in handling, the lower cost and its ease of purchase.

The main objective of this study was to develop a method using the DGT technique to analyze the labile fraction of Ba in PFW from oil (with and without treatment—intended for reuse in irrigation). Treatment consisted in processing the PFW in

sand filter. The practical goal was to establish the viability of the DGT technique as an analytical tool that could be used to evaluate the reuse of produced formation water for irrigation based on analysis of the fraction of labile Ba.

2. Experimental

2.1. Equipment and accessories

The specialized equipment and accessories used in this work were an inductively coupled plasma optical emission spectrometer (GBC Integra 2, Melbourne, Australia) equipped with a cyclonic-type spray chamber (Glass Expansion, Melbourne, Australia), a V-groove nebulizer (Precision Glassblowing, Colorado, USA) and a pH meter (Digimed, São Paulo, Brazil). The spectrometer conditions were as follows: forward power=1200 W; plasma gas flow-rate=10 L min⁻¹; auxiliary gas flow-rate=0.5 L min⁻¹; nebulizer gas flow-rate=0.6 L min⁻¹; observation height (radial viewing)=10 mm; and sample introduction flow-rate=2.8 mL min⁻¹. Measurements of Ba, K, Ca, Mg, Sr, and Na signals were performed at 493.4, 766.4, 317.9, 279.5, 421.5 and 588.9 nm, respectively. DGT polypropylene devices (piston and cap) were obtained from DGT Research Ltd., Lancaster, UK.

2.2. Reagents and solutions

The 3 MM chromatographic paper that was used as a diffusion agent and the cellulose membrane treated with phosphate (Whatman P81 membrane) that was used as the binding agent were both manufactured by Whatman (Maidstone, England). Barium standard solutions were prepared from successive dilutions of a 1010 mg L⁻¹ (1–2% w/v HNO₃) standard stock solution (Aldrich, Milwaukee, USA).

HNO₃ was purchased from Merck (Darmstadt, Germany). Solutions of NaNO₃ (Quimis, São Paulo, Brazil) and NaCl (Merck) were prepared from their respective salts. All solutions were prepared using analytical grade reagents and water purified to a resistivity of 18.2 MΩ cm.

2.3. Samples

Two samples of PFW from regions of onshore production (Natal, Rio Grande do Norte, Brazil), taken at different locations within the wastewater treatment plant (Input/Output Filter Sand), were analyzed. We also analyzed two samples from an offshore production region (Campos Basin, Rio de Janeiro, Brazil). After collection, the PFW samples were stored at 4 °C until either DGT deployment or analysis by ICP OES. For metal determination by ICP OES, the samples were filtered (0.45 μm). Concentrations of the dissolved major components for the samples are presented in Table 1.

Table 1
Concentration (mg L⁻¹) of major cations and pH in petroleum produced formation water samples.

Element	Onshore		Offshore	
	After sand filter	Before sand filter	I	II
Ca	0.866 ± 0.009	34.2 ± 0.5	6,130 ± 10	6,046 ± 509
K	39.9 ± 0.1	35.3 ± 0.9	560 ± 3	513 ± 57
Mg	3.19 ± 0.01	23.09 ± 0.04	348.1 ± 0.1	287 ± 9
Na	478 ± 4	572 ± 9	28,530 ± 110	32,360 ± 3,800
Sr	0.0340 ± 0.0003	3.23 ± 0.07	548.7 ± 1.1	574 ± 26
pH	8.61	8.97	6.37	6.33

2.4. Decontamination and conditioning of ligand and diffusive agents

Decontamination of the cellulose membrane treated with phosphate (P81 binding membrane) and used as binding agent and the chromatographic paper (3 MM) used as a diffusion layer was performed with 1 mol L^{-1} nitric acid.

After immersion in the nitric acid solution for 24 h, the binding and diffusive agents were washed with purified water until the pH of the washing solution measured between 6.5 and 7.5.

Before use, the chromatographic paper was placed in a 0.050 mol L^{-1} solution of sodium nitrate for 24 h [19].

Using plastic tweezers, the P81 binding membrane was placed on the DGT device (piston), followed by two disks of 3 MM paper, and the polypropylene sleeve was then attached to the DGT piston. To avoid contamination, the procedure was performed in a laminar flow hood.

2.5. General procedure of deployment and elution

After mounting the DGT system, the devices were deployed in standard solutions and in real samples. All immersions were conducted under controlled temperature and agitation. Short (hours) and long (> 12 h) immersions were conducted in order to verify the feasibility of using the device with different immersion periods.

After the deployments, the P81 binding membranes were removed from the device and transferred to Falcon-type conical tubes (15 mL) containing 5 mL of 2 mol L^{-1} nitric acid. The contents of the tubes were stirred for 24 h [18]; then, the membrane was removed from the tube, and the solution was analyzed by ICP OES.

3. Results and discussion

3.1. Elution factor

To evaluate the elution efficiency of the Ba retained by the ligand agent, P81 binding membranes were immersed (for 4 h) in 40 mL aliquots of a solution containing $1000 \mu\text{g L}^{-1}$ of Ba. After this sorption time, the Ba concentration remaining in the solution was measured with ICP OES. The Ba retained by the ligand agent was eluted and measured by ICP OES. By analyzing the mass retained and eluted from the binding agent, an elution factor of 0.64 ± 0.09 was obtained, which is lower than that obtained for other elements such as Ca, Mg and Na [18].

After elution, non-deployed disks presented $140 \pm 122 \text{ ng}$ of Ba. Presence of Ba in these samplers, probably, came from the eluent (2 mol L^{-1} HNO_3 analytical grade nitric acid), sodium nitrate conditioning solution (0.050 mol L^{-1}) and/or from incomplete decontamination of the membranes (P81 and/or 3 MM).

Although recovery of Ba from P81 binding membrane was relatively low, we don't test different elution procedure by considering that: optimization by increasing acid concentration from 2 mol L^{-1} HNO_3 will increase contamination of Ba from the acid; optimization by increasing agitation time will result in a very time-consuming procedure; optimisation by increasing the elution volume from 5 mL will result in excessive dilution of the eluate; recovery of 64% does not represent a practical problem to analyse real samples, since uptake of Ba can be correct by the elution factor.

3.2. Diffusion coefficient of Ba on cellulose

No information exists in the literature regarding the diffusion of Ba through paper-based membranes. Thus, the initial experiments aimed to determine the diffusion coefficient of Ba in the

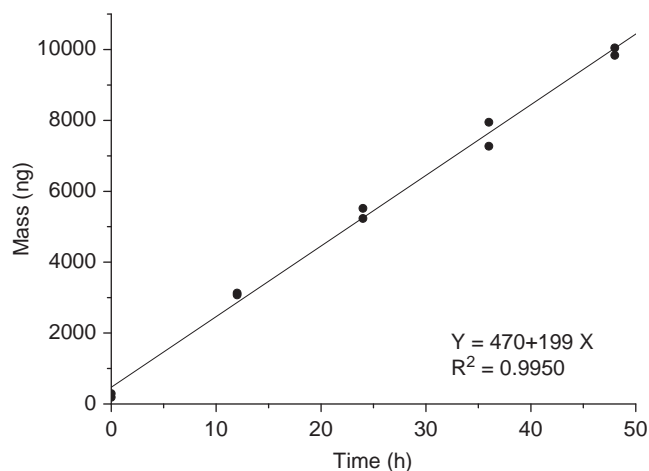


Fig. 1. Accumulated mass of Ba versus deployment time. Temperature = $23 \text{ }^\circ\text{C}$; Ba concentration = $500 \mu\text{g L}^{-1}$; $I = 0.05 \text{ mol L}^{-1}$; pH = 5.5.

diffusive layers of the cellulose used in the DGT devices. For this purpose, eight devices were immersed in 4 L of a solution containing $500 \mu\text{g L}^{-1}$ Ba (pH = 5.5 and $I = 0.050 \text{ mol L}^{-1}$ NaCl) for 0, 12, 24, 36 and 48 h. These tests were performed at $23 \text{ }^\circ\text{C}$.

Fig. 1 shows the relationship between the mass of Ba (retained by the binding agent) and the immersion time (deployment curve). A linear relationship ($R^2 = 0.995$) was observed, indicating that the interaction of Ba with the diffusive agent is insignificant and that the retention of this element by the binding agent is satisfactory. Thus, we conclude that the new DGT device is effective for the sampling of Ba in aqueous solutions under the evaluated conditions (pH = 5.5 and $I = 0.05 \text{ mol L}^{-1}$).

By applying the theory of the DGT technique [11] and determining the slope of the line plotted in Fig. 1, the diffusion coefficient (DC) of Ba on 3 MM chromatographic paper was calculated as follows:

$$D = (a\Delta g) / (CS) \quad (1)$$

where:

- S and Δg are the cross-sectional area (3.14 cm^2) and thickness of the 3 MM paper (two disks = 0.092 cm), respectively;
- C is the concentration of Ba in the deployment solution;
- a is the slope of the deployment curve (Fig. 1).

As calculated using Eq. (1), the D value was $3.22 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ($23 \text{ }^\circ\text{C}$). For comparison, a D value of $5.7 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$ ($5.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ corrected to $23 \text{ }^\circ\text{C}$) was reported [14] for Ba in polyacrylamide agarose gel associated with Chelex-100 resin (conventional sampler) with a standard deviation of 37% at pH 5.4. A similar difference in DC between conventional and alternative materials was observed for Cd, with values of 5.77 and $2.55 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ for the polyacrylamide hydrogel and the chromatographic 3 MM paper, respectively [20].

3.3. pH effect

The effect of pH on the retention of Ba is shown in Fig. 2a. This test was performed using 2 L solutions containing $500 \mu\text{g L}^{-1}$ Ba with an ionic strength of 0.05 mol L^{-1} and a deployment time of 4 h. For all pH values tested, the relative Ba concentrations were determined by dividing the concentration of Ba obtained with Eq. (1) [11] by the Ba concentration in the test solution

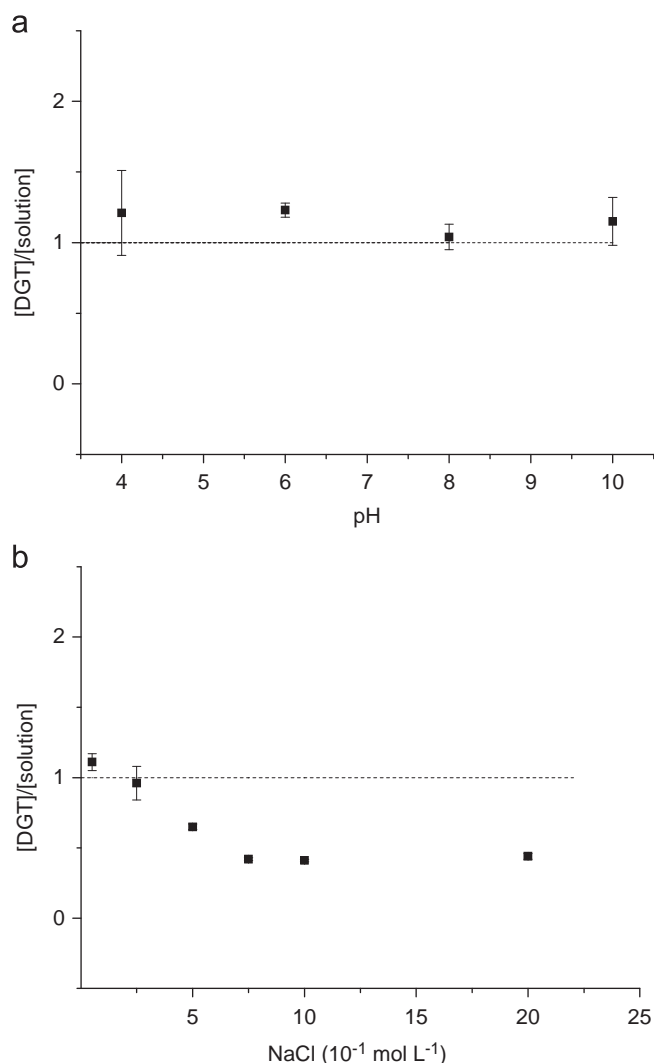


Fig. 2. Relative Ba concentration determined by DGT at various pH values (a) and NaCl concentrations (b). (a) Temperature=23 °C; Ba concentration=500 $\mu\text{g L}^{-1}$; Deployment time=4 h; $I=0.05 \text{ mol L}^{-1}$. (b) Temperature=23 °C; Ba concentration=500 $\mu\text{g L}^{-1}$; Deployment time=4 h; pH=5.5.

(500 $\mu\text{g L}^{-1}$). Fig. 2a indicates that the effect of pH on the retention of Ba is insignificant (in the range tested).

3.4. Interference of Na using the P81 membrane as binding agent

The salinity of the PFW can reach values four times higher than the salinity of oceanic waters, this corresponding to approximately 3% (approximately 0.5 mol L⁻¹ NaCl). Thus, experiments were performed to evaluate the effect of interference by Na on the Ba retention by the P81 binding membrane [2].

The interference effect of Na in the retention of Ba is shown in Fig. 2b, which shows the concentrations from deployments (4 h) of DGT devices in solutions containing 500 $\mu\text{g L}^{-1}$ Ba (pH=5.5) with different NaCl concentrations.

For NaCl concentrations equal to or lower than 0.25 mol L⁻¹, the interference effect of Na is not significant, and the use of the previously determined DC ($3.22 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$) for the quantification of Ba in these solutions is suitable.

For a NaCl concentration equal to 0.5 mol L⁻¹, the interference effect of Na becomes considerable, resulting in a significant decrease in the retained mass of Ba. This interference effect may be due to competition between Ba²⁺ and Na⁺ for the active sites of the P81 binding membrane. Compared to the 0.5 mol L⁻¹ NaCl

solutions, the effect is pronounced for the solutions with NaCl concentrations of 0.75, 1.0 and 2.0 mol L⁻¹. However, suppression of the Ba retention remains relatively constant in this concentration range (from 0.75 to 2.0 mol L⁻¹ NaCl).

3.5. Deployment curves and apparent diffusion coefficients for Ba in solution with different concentrations of NaCl

To establish the magnitude of competition between Ba²⁺ and Na⁺ for the active sites of the P81 binding membrane as a function of deployment time, experiments were performed using different concentrations of NaCl in solution (4 L) and both short and long deployment periods. Assuming that the interference effect of Na⁺ has two magnitudes (one lower for 0.5 mol L⁻¹ NaCl and another larger, however, similar for 0.75, 1.0 and 2.0 mol L⁻¹ NaCl), the immersions were performed using solutions containing 0.5 or 1.0 mol L⁻¹ NaCl. The Ba concentration in these solutions was maintained at 1000 $\mu\text{g L}^{-1}$ at pH 5.50.

The deployment curves for Ba obtained with solutions containing 0.5 and 1.0 mol L⁻¹ NaCl are presented in Fig. 3. It is evident from Fig. 3a that there is a linear increase in the retention of Ba up to four hours ($y = -2.142 + 0.040x$, where $x = \text{time [s]}$ and $y = \text{mass [ng]}$). After this time, there is a significant decrease in the retention of the analyte, and the expected curve profile for the DGT system is not maintained. Similar behavior has been reported for Cd²⁺ and Cu²⁺ in the presence of NaNO₃ [21]. For example, at NaNO₃ concentrations of 0.5 mol L⁻¹, the binding

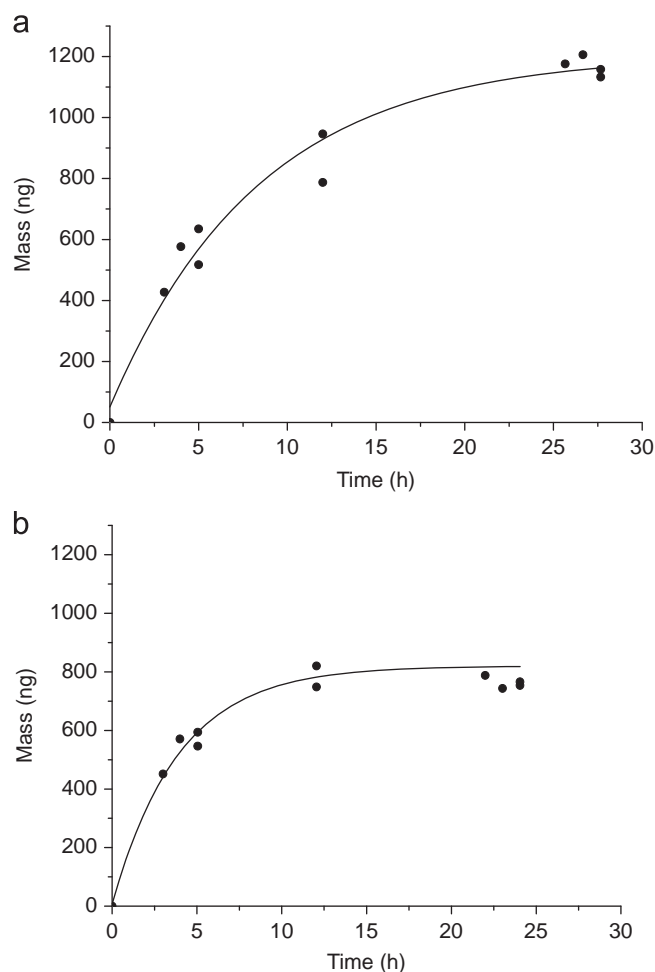


Fig. 3. Accumulated mass of Ba versus deployment time in 0.5 mol L⁻¹ (a) and 1.0 mol L⁻¹ (b) NaCl. Temperature=23 °C; Ba concentration=1000 $\mu\text{g L}^{-1}$; $I=0.50 \text{ mol L}^{-1}$; pH=5.5.

capacities for Cu^{2+} and Cd^{2+} decreased from 3.22 and 3.07 to 1.1 and 1.90 mol cm^{-2} , respectively.

Considering that the Ba retention is linear for deployment times up to four hours, we can correct the interference in the retention of the analyte using the concept of apparent diffusion coefficient (DC_{ap}). In this case, it is assumed that the sample has an ionic strength of approximately 0.5 mol L^{-1} , and we determine the concentration of Ba in the sample from the diffusion rate of the ions in the standard solution (defined as DC_{ap}). Obviously, to apply this approach, the immersions for real samples should be restricted to short periods (up to four hours). Under this assumption, the DC_{ap} obtained from the curve in Fig. 3a (linear range) was $1.43 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The results obtained with immersions of DGT devices in a solution containing 1.0 mol L^{-1} NaCl are shown in Fig. 3b. The system behavior was similar to that observed for 0.5 mol L^{-1} NaCl, showing a linear increase up to approximately 4–5 h ($y=3.589+0.040x$, where $x=\text{time [s]}$ and $y=\text{mass [ng]}$), followed by a plateau after 5 h. In this case, the DC_{ap} obtained from the linear part of the curve in Fig. 3b was $9.9 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$.

The values for the apparent diffusion coefficients of the 1.0 and 0.5 mol L^{-1} NaCl solutions were approximately 30 to 45% of the real diffusion coefficients obtained from 0.05 mol L^{-1} NaCl solutions, respectively. Similar behavior is apparent from the data in Fig. 2: the values for the apparent diffusion coefficients of the 1.0 and 0.5 mol L^{-1} NaCl solutions were approximately 40–60% of the real diffusion coefficients obtained from the 0.05 mol L^{-1} NaCl solutions. The small (c.a. 15%) difference between these two sets of data is attributed to imprecision in the DGT measurement.

3.6. Deployment curves in petroleum produced formation water samples

The curve obtained by the deployment of DGT paper-based devices in a sample of PFW (onshore) collected after the entrance of the sand filter are shown in Fig. 4a. Fig. 4b shows the curve obtained for a sample of PFW (onshore) collected before the entrance of the sand filter. For both curves, there is a linear relationship ($R^2=0.9825$ and 0.9881), suggesting no interference on the retention of Ba. Tables 2 and 3 list the dissolved concentrations of Ba determined by DGT (for various immersion times) and the total concentration of dissolved Ba determined by ICP OES in the samples of produced formation water. To determine the concentration of Ba by DGT, Eq. (1) [11] was used. Based on the concentrations of Na, which is the main component of the sample (Table 1), it was assumed for these two samples of PFW that there is no interference of Na on Ba, and therefore, the DC value obtained with Ba solutions where $I=0.05 \text{ mol L}^{-1}$ was used for the calculations of the concentrations.

Tables 2 and 3 show that the results were consistent with the expected values. For both samples (collected before and after the entrance of the sand filter), the mean concentrations of Ba obtained by DGT were not significantly different from those obtained by ICP OES (total Ba concentration). Thus, we can conclude that there is no non-labile Ba (for example, BaCO_3 and BaSO_4) in these samples. For comparison, Jackson and Reddy [22] reported the following species for dissolved Ba in coal bed natural gas produced water: Ba^{2+} (89–97%) and BaHCO_3^+ (3–11%).

Fig. 5 shows the deployment curve for a sample of produced formation water resulting from offshore extraction (sample I). The curve has a behavior highly similar to that obtained for the solution containing Ba and 1 mol L^{-1} NaCl. This behavior was expected given the concentration of Na in this sample (Table 1). Thus, to assess the Ba concentration in this sample, the diffusion coefficient obtained with the solution containing Ba and 1.0 mol L^{-1} NaCl was used. The calculations were restricted to

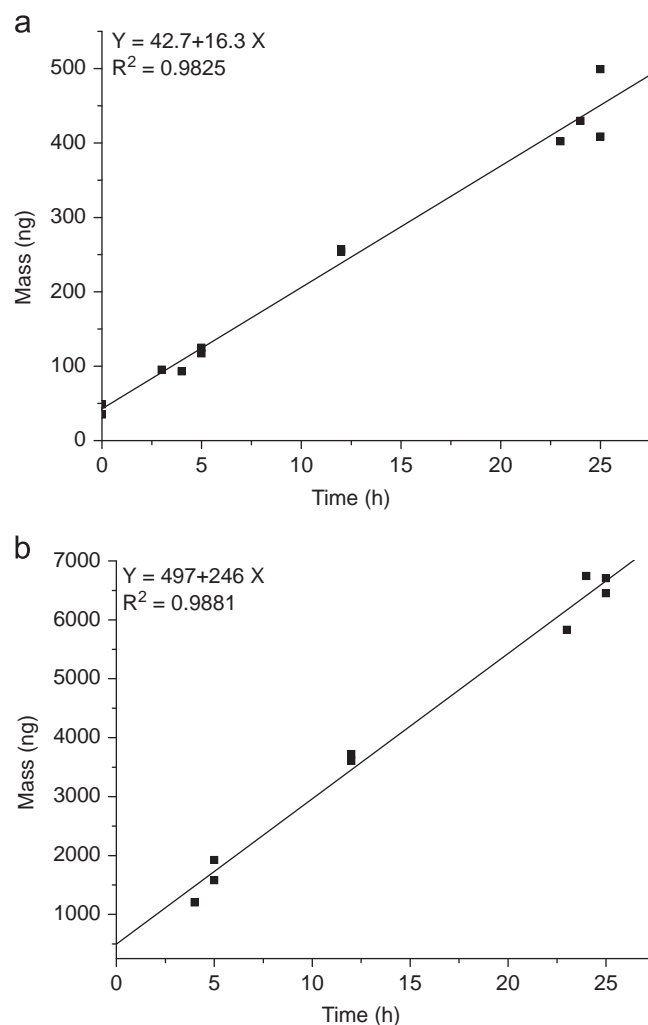


Fig. 4. Accumulated mass of Ba versus deployment time in a sample of petroleum produced formation water (onshore) collected after (a) and before (b) the sand filter. (a). Temperature= $23 \text{ }^\circ\text{C}$; Ba concentration= 35 ng mL^{-1} ; pH= 8.97 . (b). Temperature= $23 \text{ }^\circ\text{C}$; Ba concentration= 760 ng mL^{-1} ; pH= 8.61 .

Table 2

Labile concentrations of Ba (determined by using DGT) in a petroleum produced formation water (onshore) sample collected after sand filter. Total Ba concentration: 0.035 mg L^{-1} .

Deployment time (h)	[Ba] DGT (mg L^{-1})
3	0.045
4	0.032
5	0.042
5	0.038
12	0.045
12	0.045
23	0.040
24	0.041
25	0.046
25	0.037
^a Mean \pm SD	0.041 ± 0.005

^a $n=10$.

short immersions, which provide a linear response between immersion time and accumulated mass ($y=61.1+833x$, $R^2=0.9841$, where $x=\text{time [h]}$ and $y=\text{mass [ng]}$). The results obtained with this approach are presented in Table 4. The Ba concentrations obtained for this sample were lower than

Table 3

Labile concentrations of Ba (determined by using DGT) Ba in a petroleum produced formation water (onshore) sample collected before sand filter. Total Ba concentration: 0.760 mg L⁻¹.

Deployment time (h)	[Ba] DGT (mg L ⁻¹)
4	0.758
5	0.797
5	0.971
12	0.758
12	0.782
23	0.640
24	0.709
25	0.651
25	0.677
^a Mean ± SD	0.75 ± 0.1

^a n=9.

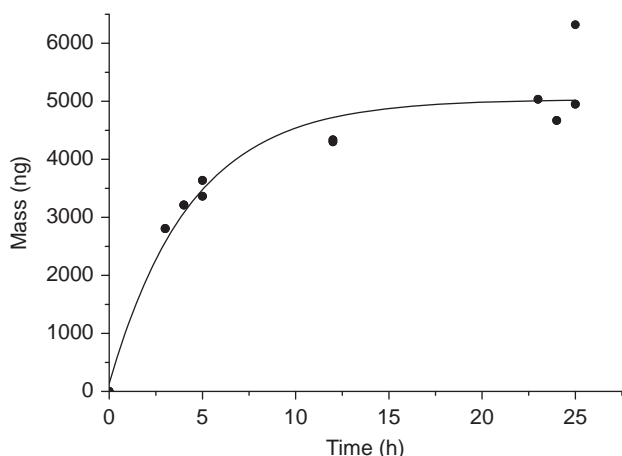


Fig. 5. Accumulated mass of Ba versus deployment time in a sample of petroleum produced formation water (offshore). Temperature=23 °C; Ba concentration=9.48 µg mL⁻¹; pH=6.37.

Table 4

Labile (determined by using DGT) and total (determined directly by ICP OES) concentrations of Ba in a petroleum produced formation water (offshore I). Total Ba concentration: 9.48 mg L⁻¹.

Deployment time (h)	[Ba] DGT (mg L ⁻¹)
3	7.69
4	6.59
^a Mean ± SD	7.1 ± 0.8

^a n=2.

(although similar to) the dissolved Ba concentration, which can be attributed to the calibration procedure because it only considers the presence of Na in the sample. Interference from alkaline earth cations (Ca) may be the reason for the relatively low recovery of Ba in this sample. However, the existence of non-labile Ba species, such as BaCO₃ and BaSO₄, is also a possibility.

To confirm the new analytical approach for Ba determination, another PW sample (offshore II) was analyzed by using deployment time of 2, 3 and 4 h. The deployment curve was characterized by a linear relationship ($y=192+430x$, $R^2=0.9353$, where x =time [h] and y =mass [ng]). Table 5 compares the concentration of Ba determined by using DGT and ICP OES. There is no significant difference between those values. Thus, we can conclude that there is no non-labile Ba in this sample. Also, results for

Table 5

Labile (determined by using DGT) and total (determined directly by ICP OES) concentrations of Ba in a petroleum produced formation water (offshore II). Total Ba concentration: 4.7 mg L⁻¹.

Deployment time (h)	[Ba] DGT (mg L ⁻¹)
2 ^a	4.93
3 ^a	4.75
4 ^a	3.87
^b Mean ± SD	4.5 ± 0.6

^a n=2.

^b n=6.

sample II shows that interference from Ca on uptake of Ba is negligible.

4. Conclusions

A new method for the determination of Ba using paper-based DGT samplers was established. The 3 MM diffusive agent and the P81 binding agent can be used for the sampling of Ba in petroleum-produced formation water (onshore) samples that have a salinity of less than 0.5 mol L⁻¹ NaCl. The primary interference effect on the DGT technique for the sampling of Ba was salinity, which directly influences the retention of Ba by the P81 binding agent. A procedure to reduce this interference (in samples containing high levels of sodium, from 0.5 to 1 mol L⁻¹ NaCl) was proposed that is based on the use of an apparent diffusion coefficient. This procedure was suitable for analyzing water with high salt concentrations (derived from petroleum extraction in offshore Campos Basin, RJ) and is potentially useful for in situ analysis; however, the immersion time was limited to 4 h.

Acknowledgments

The authors thank the Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for their financial support.

References

- [1] M.T. Stephenson, Produced Water Technological/Environmental Issues and Solutions, in: J.P. Ray, F.R. Engelhardt (Eds.), Plenum Press, New York, 1992, pp. 1–9.
- [2] I.T. Gabardo, (March 2007). Caracterização química e toxicológica da água produzida descartada em plataformas de óleo e gás na costa brasileira e seu comportamento dispersivo no mar. Retrieved December 15, 2010 from <http://bdttd.bczm.ufrn.br/tedesimplificado/tde_arquivos/35/TDE-2007-11-22T060337Z-938/Publico/IreneTG.pdf>.
- [3] R. Suwa, K. Jayachandran, N.T. Nguyen, A. Boulouvar, K. Fujita, H. Saneoka, Arch. Environ. Contam. Toxicol. 55 (2008) 397–403.
- [4] M. Llugany, C. Poschenrieder, J. Barcelo, Arch. Environ. Contam. Toxicol. 39 (2000) 440–444.
- [5] A. Oskarsson, A.L. Reeves, Handbook on the Toxicology of Metals, in: G. Nordberg, B. Fowler, M. Nordberg, L. Friberg (Eds.), Academic Press, Maryland Heights, 2007, pp. 407–414.
- [6] I. Muhammad, M. Puschenreiter, W.W. Wenzel, Sci. Total Environ. 416 (2012) 490–500.
- [7] P.N. Williams, H. Zhang, W. Davison, A.A. Meharg, M. Hossain, G.J. Norton, H. Brammer, M.R. Islam, Environ. Sci. Technol. 45 (2011) 6080–6087.
- [8] I. Ahumada, L. Ascar, C. Pedraza, V. Vásquez, A. Carrasco, P. Richter, S. Brown, Water Air Soil Pollut. 219 (2011) 225–237.
- [9] J.M. Soriano-Dista, T.W. Speir, I. Gómez, L.M. Clucas, R.G. McLaren, J. Navarro-Predreño, Water Air Soil Pollut. 213 (2010) 471–483.
- [10] M. Schintu, B. Marras, L. Durante, P. Meloni, A. Contu, Environ. Monit. Assess. 167 (2010) 653–661.
- [11] H. Zhang, W. Davison, Anal. Chem. 67 (1995) 3391–3400.

- [12] H. Zhang, W. Davison, *Environ. Chem.* 9 (2012) 1–13.
- [13] J. Gimpel, H. Zhang, W. Davison, A.C. Edwards, *Environ. Sci. Technol.* 37 (2003) 138–146.
- [14] O.A. Garmo, O. Ryset, E. Steinnes, T.P. Flaten, *Anal. Chem.* 75 (2003) 3573–3580.
- [15] W. Li, H. Zhao, P.R. Teasdale, R. John, F. Wang, *Anal. Chim. Acta* 533 (2005) 193–202.
- [16] L.Y. Chang, W. Davison, H. Zhang, M. Kelly, *Anal. Chim. Acta* 368 (1998) 243–253.
- [17] W. Li, F. Wang, W. Zhang, D. Evans, *Anal. Chem.* 81 (2009) 5889–5895.
- [18] W. Li, H. Zhao, P.R. Teasdale, R. John, S. Zhang, *Anal. Chim. Acta* 464 (2002) 331–339.
- [19] B.L. Larner, A.J. Seen, *Anal. Chim. Acta* 539 (2005) 349–355.
- [20] A.A. Menegário, P.S. Tonello, S.F. Durrant, *Anal. Chim. Acta* 683 (2010) 107–112.
- [21] W. Li, H. Zhao, P.R. Teasdale, R. John, S. Zhang, *Anal. Chim. Acta* 464 (2002) 331–339.
- [22] R.E. Jackson, K.J. Reddy, *Environ. Sci. Technol.* 41 (2007) 5953–5959.