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In situ redox speciation analysis of chromium in water by diffusive gradients in thin films using a DE81 anion exchange membrane

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ABSTRACT

A method for the *in situ* redox speciation analysis of chromium in water by the diffusive gradients in thin films (DGT) technique using a DE81 anion exchange membrane was successfully developed. For the selective uptake of Cr(VI), a DGT device containing an anion exchange membrane DE81 (cellulose acetate chromatographic paper) was used (DE81-DGT), while selective uptake of Cr(III) was carried out using DGT devices containing the Chelex-100 resin (Chelex-100-DGT). A correlation coefficient of 0.993 was obtained for the linearity of the immersion curves (mass *versus* time) using DE81-DGT. The diffusion coefficient values for Cr(VI) through the agarose diffusive layer were equal to $4.89 \pm 0.5 \times 10^{-6}$ cm^2 s^{-1} and $3.95 \pm 0.02 \times 10^{-6}$ cm^2 s^{-1} (T=23 ± 1 °C, I=0.03 mol L^{-1} $NaNO_3$) were obtained by using diffusion cell and immersion curves, respectively. The retention of Cr(VI) by the DE81 membrane in a synthetic sample and river water was not affected by the pH over a wide range 4–9). Recoveries of Cr(VI) between 90% and 120% from solutions of ionic strength ranging from 0.01 to 0. 5 mol L^{-1} $NaNO_3$ were achieved. Finally, the redox speciation analysis of Cr(III) and Cr(VI) in spiked river water and synthetic samples was performed with recoveries greater than 80% and 87% by using Chelex-100-DGT and DE81-DGT devices, respectively. Those results were in excellent agreement with the diphenylcarbazide spectrophotometric method.

1. Introduction

Chromium is widely distributed in the environment due to its various industrial applications such as electroplating, chromium-based pigments, mining, leather tanning and chromium alloy production [1,2]. It commonly exists in two oxidation states in natural water systems: trivalent chromium Cr(III) and hexavalent chromium Cr(VI) [1]. While Cr(III) is considered an essential human nutrient (with some exceptions in recent studies) [3], Cr(VI) is well known as being harmful to human health[1]. Chromium speciation has been extensively studied, mainly in drinking water. One of the main reasons for this is the low maximum concentration level of total chromium in drinking water (50 μg L^{-1}) recommended by the World Health Organization, in addition to its known health effects [4]. The maximum permissible concentrations of these chromium species in wastewater have been established at 1 mg L^{-1} for Cr(III) and 0.1 mg L^{-1} for Cr(VI) [5]. Thus, it becomes extremely necessary to develop reliable methods for these determination of chromium species in water [2].

Developed in the early 1990s [6,7], the diffusive gradients in thin film (DGT) technique appears to be a powerful tool for speciation analysis. This technique offers the possibility of selective *in situ* sampling of the species [7,8], avoiding the necessity of sample storage. By using a simple relation (Eq. (1)), this technique allows the calculation of the time-integrated concentration of analytes during the sampling time. A DGT device consists of a diffusive gel disc (commonly a polyacrylamide-agarose gel) used as a diffusion layer of known thickness (Δg) and diffusion area (A) over a binding layer (Chelex-100 impregnated in a polyacrylamide gel). Therefore, after determining the accumulated mass (M) of the analyte in the binding layer, it is possible to calculate the average concentration of the analyte in the field sample studied because we already know the analyte diffusion coefficient through the gel (D) and the exposure time (t).

$$C = M\Delta g\,(D\,t\,A)^{-1} \quad (1)$$

To date, only a few approaches for the determination of the Cr redox species by DGT rigorously matched the IUPAC [9] definition of speciation analysis. The Chelex-100 binding layer for Cr(III) with

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no retention of Cr(VI) [10] is based on combining a DGT for the selective retention of Cr(III) and the diffusive equilibrium in thin films (DET) for the selective uptake of Cr(VI) on a diffusive layer. Additionally, a polyquaternary ammonium salt liquid binding layer and a dialysis membrane as the diffusive layer has been proposed for Cr(VI) [11]. In both approaches, only one species was retained in the binding phase and can thus be pre-concentrated. N-methyl-D-glucamine (NMDG) has been recently proposed as a DGT ligand (NMDG-DGT) to sample Cr(VI) *in situ*. This method was evaluated for natural fresh water and was able to pre-concentrate Cr(VI) even in the presence of a ten-fold greater Cr(III) concentration. However, this method is limited by ionic strength (I) which ranges from 0.0001 to 0.075 mol L^{-1} [12].

The binding phase sodium poly(aspartic acid) (PASP) and poly (quaternary ammonium) salt (PQAS) were used for the speciation of Cr(III) and Cr(VI) using DGT. The concentration of Cr(VI) was determined by a DGT device with the PQAS salt solution and Cr(III) was determined by a DGT device with the PASP solution. The proposed approach was evaluated for the analysis of tap water. Recoveries of the spiked Cr(VI) and Cr(III) were 98.2–107.7% and 97.9–105.3%, respectively[13].

In this work, the chemical speciation of Cr(VI) and Cr(III) in river water was performed for the first time with the DGT technique using a diethylaminoethyl acetate anion exchange membrane (DE81) for the selective retention of Cr(VI) in combination with an earlier-reported [10] approach to retain Cr(III) in the Chelex-100 binding layer.

2. Materials and methods

2.1. Reagents

All reagents used were from an analytical grade. Solutions were prepared with ultrapure water with a resistivity of 18 MΩ cm^{-1} (Milli-Q, Millipore Academic, USA). The DGT devices and Chelex-100 binding gels were purchased from DGT Research Ltd. (Lancaster, UK). The cellulose acetate membrane filters (25-mm diameter, 0.45-μm pore size and 0.13-mm thickness) were purchased from GVS Filter Technology. The Whatman® DE81 cellulose paper with a weak basic anion exchanger, diethylaminoethyl functional groups (1.7 μeq cm^{-2}, 0.20 mm) was obtained from GE Healthcare Life Science. Diffusive gels were prepared with Agarose RA™, biotechnology grade (AMRESCO, USA).

2.2. Methods

The determination of total chromium was carried out by inductively coupled plasma optical emission spectrometry (ICP-OES) using an iCAP™ 6000 Series (Thermo Scientific™, Germany). The ICP-OES operating conditions are listed in Table 1. Additionally, a DR 2800™ Portable Spectrophotometer (Hach Company, USA) was employed to measure Cr(VI) by the diphenylcarbazide method[14].

All DGT devices, diffusion cells and other plastic components used in this work were cleaned by immersing in a 20% (v/v) HNO_3 solution for a period of 4 h and then rinsing with ultrapure water. The DE81 membrane and cellulose acetate membrane were decontaminated with nitric acid solution (10%, v/v) for 24 h. After that, the membranes were washed with ultrapure water in order to removing acid residues until pH of the wash water reached values of about pH 5–6. Agarose diffusive gels were prepared similarly as previously described [15]. The cellulose acetate membranes and the agarose diffusive gels were stored in a 0.03 mol L^{-1} sodium nitrate solution and the DE81 membrane was stored in ultrapure water at 4 °C.

Table 1
ICP-OES operating conditions.

Operating parameters	Units	Axial
RF power	(W)	1,150
Gas flow rate	(L min^{-1})	0.7
Auxiliary gas flow rate	(L min^{-1})	0.5
Sample flow rate	(mL min^{-1})	2
Nebulization chamber		Cyclonic
Nebulizer		V-Groove
Emission line	(nm)	267.72

2.2.1. Elution factor of Cr(VI) from the DE81 membrane

To determine the uptake and elution efficiency of Cr(VI) from the DE81 membrane, three DE81 membrane discs were placed in a vessel containing 250 mL of 30 μg L^{-1} Cr(VI) solution with an ionic strength of 0.03 mol L^{-1} $NaNO_3$ and pH=6.1. The DE81 membrane discs were removed after 12 h and eluted with 3 mL of 10% (v/v) nitric acid with stirring for 24 h. The elution factor (f_e) was calculated according to Eq. (2),

$$f_e = M_e M_r^{-1} \quad (2)$$

where M_e is the eluted mass of Cr(VI) from the DE81 membranes and M_r is the retained mass. The retained mass was calculated from the difference between the concentration of the solution before and after the immersion of DE81 membranes.

2.2.2. Diffusion coefficient measurements

The diffusion coefficient of Cr(VI) was determined by both the diffusion cell and deployment curve methods. The diffusion cell method, as previously reported [16,17], was carried out by preparation of two solutions, A and B, with equal ionic strength (0.03 mol L^{-1} $NaNO_3$ and pH=5.6). Solution A was prepared with no addition of Cr(VI) while solution B was prepared to contain 5 mg L^{-1} of Cr(VI). During a period of 2 h, 1 mL was collected from solution A every 15 minutes and acidified with nitric acid solution (2%, v/v). For the deployment curve method, 4 L of 60 μg L^{-1} Cr(VI) solution (I=0.03 mol L^{-1} $NaNO_3$, pH=5.6 at 23 ± 1 °C) were prepared. The DGT devices were assembled and placed into the solution. These DGT devices were retrieved in duplicate after 2, 4, 6, 8 h and the Cr(VI) was eluted from the discs as described above. The diffusion coefficient (D, cm^2 s^{-1}) was obtained by Eq. (3),

$$D = a\,\Delta g\,(AC_s)^{-1} \quad (3)$$

where **a** is the slope obtained by plotting the mass (ng) of Cr(VI) *versus* time (ng s^{-1}); Δ**g** is the gel thickness (0.013 cm cellulose acetate membrane plus 0.08 cm agarose diffusive gel thicknesses); **A** (cm^2) is the exposed area of the gel in the DGT devices (3.14 cm^2) or in the diffusion cell (1.77 cm^2); $\mathbf{C_s}$ is the Cr(VI) concentration of the deployment solution or concentration of solution B.

2.2.3. pH and ionic strength

To evaluate the influence of pH on Cr(VI) uptake by the DE81 membrane, five solutions (1 L) containing 100 μg L^{-1} Cr(VI) (I=0.03 mol L^{-1} $NaNO_3$) were prepared and the pH was adjusted to 4.0, 5.0, 6.0, 7.0 or 9.0. Similarly, to evaluate the ionic strength

Table 2
Physical and chemical parameters of the synthetic samples (Mean ± SD, n=3).

Solutions	Cr species	Conductivity (mS cm^{-1})	pH
1	Cr(III)	2.63 ± 0.01	5.4 ± 0.2
2	Cr(VI)	2.64 ± 0.04	5.4 ± 0.2
3	Cr(III) + Cr (VI)	2.64 ± 0.03	5.4 ± 0.2

Table 3
Physical and chemical parameters measured in the Piracicaba river sample (Mean ± SD, n=3).

Conductivity	($\mu S\ cm^{-1}$)	515 ± 2
[a] I	(mol L^{-1}) × 10^{-3}	6.50 ± 0.03
[b] TDS	(mg L^{-1})	330 ± 1
[c] TOC	(mg L^{-1})	7.13 ± 0.16
T	(°C)	23.5 ± 0.7
Eh	(V)	0.195 ± 0.001
pH		7.9 ± 0.04
HCO_3^-	(mg L^{-1})	85
F^-	(mg L^{-1})	0.29
Cl^-	(mg L^{-1})	47
NO_2^-	(mg L^{-1})	0.40
NO_3^-	(mg L^{-1})	30
PO_4^{3-}	(mg L^{-1})	0.94
SO_4^{2-}	(mg L^{-1})	56

[a] I = ionic strength, values calculated according Griffin and Jurinak (1973) [18].
[b] TDS = total dissolved solids.
[c] TOC = total organic carbon.

effect, four flasks containing 1 L of 100 μg L^{-1} Cr(VI) solutions were prepared (pH=5.6). For the individual flasks, ionic strengths were 0.005, 0.01, 0.03 and 0.5 mol L^{-1} $NaNO_3$. Both experiments were carried out in duplicate at 23 ± 1 °C. The DGT devices were deployed and retrieved after a deployment period of 6 h.

2.2.4. Redox speciation of chromium using DGT technique

Synthetic samples and a river water sample containing Cr(III) and/or Cr(VI) were used to evaluate the efficiency of the proposed approach for redox speciation analysis of chromium. Tables 2 and 3 show the physical and chemical parameters of the synthetic sample and the Piracicaba river sample, respectively, measured during speciation analysis. The ionic strength was calculated according to previous work [18]. Two DGT devices containing DE81 membrane discs and two containing Chelex-100 resin discs were immersed in solutions and in the Piracicaba river sample for 6 h.

The diffusion gel used for the DGT devices containing DE81 membrane discs was agarose gel 1.5% (w/v) and for DGT devices containing Chelex-100 discs was polyacrylamide gel cross-linked with an agarose derivative purchased from DGT Research Ltd., UK.

The Chelex-100 resin gel (also purchased from DGT Research Ltd.) was washed with ultrapure water to remove excess solution. The elution of Cr(III) from Chelex-100 discs was performed with 1 mL of HNO_3 (1 mol L^{-1}). The discs were shaken using an orbital shaker (Labnet Instruments, Inc., USA) for a period of 24 h.

The elution factor used for elution of Cr(III) from the Chelex-100 resin was 0.79 ± 0.06 [10], and diffusion coefficient was 4.50×10^{-6} $cm^2\ s^{-1}$ [16].

3. Results and discussions

3.1. Elution factor and Cr(VI) diffusion coefficient

An elution factor of 0.89 ± 0.01 was obtained using Eq. (2). This value is better than those reported for other binding phases, such as the elution efficiency of 0.79 ± 0.07 for Cr(III) on Chelex-100[10] and is similar to the elution factor (0.88) obtained for U when using a DE81 membrane [19].

The diffusion coefficient for Cr(VI) in the agarose gel (I=0.03 mol L^{-1} $NaNO_3$ and pH=5.6 at 23 ± 1 °C) was $4.89 \pm 0.5 \times 10^{-6}$ $cm^2\ s^{-1}$obtained by the diffusion cell method (from a linear relationship with a slope of 0.893 ng s^{-1} and R^2 between 0.96 and 0.97).

The accumulated mass of Cr(VI) in the DGT devices containing DE81 membrane *versus* time showed a linear behaviour (characterized by an R^2=0.993) during the immersion time (Fig. 1), demonstrating the capacity of the proposed material to be used as the binding layer for the DGT technique for sampling Cr(VI). From these data and Eq. (3), a diffusion coefficient of $3.95 \pm 0.02 \times 10^{-6}$ $cm^2\ s^{-1}$ was obtained in agarose gel (I=0.03 mol L^{-1} $NaNO_3$, pH=5.6 at 23 ± 1 °C). This value is similar to that obtained by the diffusion cell.

By comparison, Chen et al. [11] have reported a value of $D=2.91 \pm 0.12 \times 10^{-7}$ $cm^2\ s^{-1}$ for Cr(VI) in a dialysis membrane, 16% lower than the value obtained in the present method. On the other hand, Pan et al. [12] reported a 51% higher diffusion coefficient value for a polyacrylamide hydrogel.

The value of $3.95 \pm 0.02 \times 10^{-6}$ $cm^2\ s^{-1}$ was assumed as the diffusion coefficient for further experiments. In a solid-phase extraction test (batch mode), the average of the masses of Cr(VI) retained by a DE81 disc was 653.50 ± 12.26 ng (12 h of immersion). Because the mass of one DE81 disc is 0.0403 ± 0.0004 g, the exchange capacity (EC) value obtained for the binding material

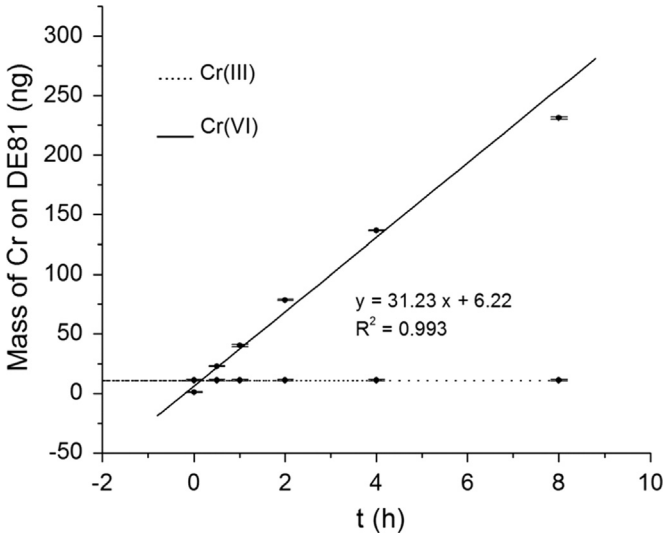

Fig. 1. Deployment curve obtained by using the DE81 membrane. Deployment solution 60 μg L^{-1} Cr(VI) (I=0.03 mol L^{-1} $NaNO_3$, pH=5.6, 23 ± 1 °C); n=2; Mean ± SD.

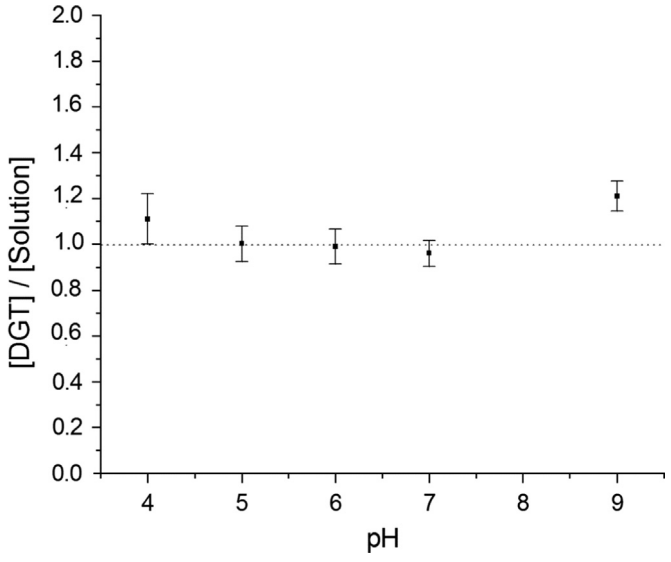

Fig. 2. Influence of pH on the Cr(VI) uptake by the DE81 membrane. Deployment solution containing 100 μg L^{-1} of Cr(VI); I=0.03 mol L^{-1} $NaNO_3$ at 24 ± 0.5 °C; deployment time=6 h; n=3; Mean ± SD.

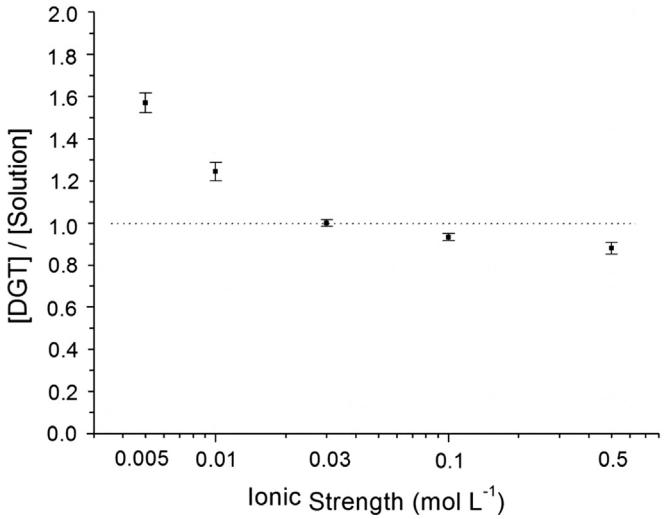

Fig. 3. Influence of I on the Cr(VI) uptake by the DE81 membrane. Deployment solution containing 100 μg L^{-1} Cr(VI); 23 ± 1 °C; deployment time = 6 h; n = 3. Mean ± SD.

was 16.22 ± 0.30 μg g^{-1} (n = 3). Based on these comments, it can be seen from Fig. 1 that the total capacity of retained Cr(VI) was not attained in a time period of 8 h.

Considering the slope of the immersion curve, a mass of 31.23 ng of Cr(VI) is retained per hour from a solution containing 59 (± 1.5) μg L^{-1} Cr(VI). Assuming a Cr(VI) concentration of 1 ng mL^{-1} in the aquatic system a deployment of 96 h (four days) will take 59.9 ng of Cr. This value represents only 9% of the exchange capacity of the binding layer.

3.2. Effect of pH and ionic strength on Cr(VI) uptake

The uptake of Cr(VI) by the DE81 was independent of the solution pH over the entire studied pH range (4–9) (Fig. 2) because the $HCrO_4^-$ and CrO_4^{2-} anionic species of Cr(VI) occur in this pH range. This result is in agreement with that reported in a previous study [11,12].

The results obtained showed that the Cr(VI) uptake by DE81 was almost unaffected by ionic strength in the range of 0.01–0.5 mol L^{-1} with recoveries between 88% and 120% (Fig. 3). However, for an ionic strength value of 0.005 mol L^{-1} $NaNO_3$, the diffusion of Cr(VI) experienced an increase. This resulted in an overestimated concentration measured by DGT approximately 60% higher than the actual value. Similar results were earlier reported for other ions and diffusive layers [20]. Pan et al. [12] reported a range of ionic strength from 0.0001 to 0.075 mol L^{-1} for Cr(VI) that could be useful for lower ionic strength water systems. On other hand, the proposed approach could be applied to water systems with higher ionic strength.

For higher ionic strength values (0.5 mol L^{-1}), a small decrease was observed in the Cr(VI) mass retained on DE81 of up to 20% (Fig. 3). This behaviour may happen because of the competition of the NO_3^- and Cr(VI) ions by the DE81 binding sites, as reported for DE81 on the uptake of U anions [19] (for a polyacrylamide hydrogel).

3.3. Selective measurement of Cr(VI) and speciation analysis of Cr (VI) and Cr(III)

Satisfactory recoveries (greater than 87% of Cr(VI)) and a low uptake of Cr (III) (less than 17%) from the synthetic sample were obtained for the DE81 binding layer (Table 4), indicating the potential for its use in the selective measuring for Cr(VI) by DGT. Additionally, at this point, it is important to keep in mind that the DE81 membrane has approximately 85% of water (0.22 mL of H_2O) when hydrated. Therefore, part of the 17% of the Cr(III) inside the membrane came from the mass of Cr(III) in equilibrium with the bulk solution and was not linked to the functional group of the DE81 membrane. As the amount of Cr(III) in the binding membrane coming from equilibrium with the bulk solution is constant, this amount can be considered as insignificant when a longer deployment time is used. This fact can be clearly observed in Fig. 1. Assuming that the DE81 contains 0.22 mL of H_2O and is exposed to a 50 ng mL^{-1} solution of Cr(III), the mass of Cr(III) present in one DE81 disc due to diffusional equilibrium is equal to 11.01 ± 0.53 ng, which corresponds to less than 5% the mass of Cr (VI) retained on the DE81 after 8 h of deployment (Fig. 1) from a solution containing approximately 50 to 60 ng mL^{-1} Cr(VI). On other hand, this value can be increased to approximately 40% when 1 h of deployment is used. As a comparison, Pan et al. [12] reported a 5% residual mass of Cr(III) out of the total retained mass of Cr(VI) after 72 h of deployment.

Furthermore, as previously reported [10], the Chelex-100 resin has been demonstrated as inadequate for the uptake Cr(VI), showing recoveries of approximately 20%, in contrast to recoveries of 80% for Cr(III), as shown in Table 4. These results were consistent with the direct measurement of total Cr determined by ICP-OES.

The proposed method was also effective for chromium speciation in synthetic sample as well in spiked river water. Results obtained by combining the spectrophotometric method (for selective determination of Cr(VI)) with ICP-OES were in good agreement with the proposed method for the redox speciation analysis of chromium for both synthetic samples and spiked river waters (Table 4).

Compared to the previous method based on combining DGT for the determination of Cr(III) with DET for the determination of the Cr(VI) concentration [10], the proposed approach allows for improvement in the LOD for the determination of Cr(VI) because this species can also be pre-concentrated. For example, when determining Cr(VI) by using DET and ICP-OES (axial view) a LOD of

Table 4
Concentrations of Cr(VI) and Cr(III) measured in synthetic and river samples by the proposed approach. (Mean ± SD, μg L^{-1}, n = 3).

Sample		DGT			ICP-OES	Colorimetry	
		[Chelex]	[DE81]	[Total] [a]	[Total]	[Cr (VI)]	[Cr (III)] [b]
1	Cr(III)	37 ± 2	9 ± 1	46 ± 2	42 ± 1	6 ± 1	35 ± 1
2	Cr(VI)	9 ± 1	47 ± 2	56 ± 2	54 ± 1	54 ± 1	< LD [c]
3	Cr(III/VI)	40 ± 1	53 ± 2	93 ± 2	97 ± 1	54 ± 1	43 ± 1
4	Piracicaba River [d]	31 ± 1	59 ± 1	89 ± 1	85 ± 1	53 ± 1	32 ± 1

[a] Obtained by sum of [Chelex] + [DE81].
[b] Obtained by subtracting [Total] (obtained by ICP-OES) and [Cr(VI)] (obtained by spectrophotometry).
[c] $LD_{ICP\text{-}OES}$ = 0.6 μg L^{-1}.
[d] Spiked with Cr(III) and Cr(VI).

0.6 ng mL^{-1} can be estimated. This LOD can be improved to approximately 0.04 ng mL^{-1} (for a deployment time of four days) when using the proposed approach associated with ICP-OES. The LOD was estimated considering the instrumental LOD of ICP and the pre-concentration factor (15 for a deployment time of four days) obtained by the proposed approach. Additionally, the proposed method compared to the previous DGT methods used for selective retention of Cr(VI) [11] avoids the use of DGT devices based on a time consuming and more expensive liquid binding layer.

4. Conclusions

For the first time, DE81 weak-anion-exchange discs, as used as the binding layer, were evaluated for the selective and quantitative retention of Cr(VI).

The proposed approach can be successfully applied *in situ* for selective Cr(VI) measurements in freshwater with a pH range from 4 to 9 and an ionic strength from 0.005 to 0.5 mol L^{-1} $NaNO_3$.

The redox speciation analysis of chromium using DGT was effectively performed by combining the selectivity of a DE81 membrane for Cr(VI) and the selectivity of Chelex-100 for the Cr (III) species.

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