ELSEVIER

Determination of iron(III) in water samples by microsequential injection solid phase spectrometry using an hexadentate 3-hydroxy-4-pyridinone chelator as reagent

Joana L.A. Miranda[a], Raquel B.R. Mesquita[a,b], Ana Nunes[b], Maria Rangel[b], António O.S.S. Rangel[a,*]

[a] Universidade Católica Portuguesa, CBQF - Centro de Biotecnologia e Química Fina – Laboratório Associado, Escola Superior de Biotecnologia, Rua Arquiteto Lobão Vital 172, 4200-374 Porto, Portugal
[b] REQUIMTE - LAQV, Instituto de Ciências Biomédicas de Abel Salazar, Universidade do Porto, Rua Jorge Viterbo Ferreira, 228, 4050-313 Porto, Portugal

ARTICLE INFO

ABSTRACT

In this work, the hexadentate 3,4–hydroxypyridinone ligand was used as reagent for the spectrophotometric quantification of iron(III) in fresh and sea waters, using a micro sequential injection lab-on-valve (μSI-LOV) system in a solid phase spectrometry (SPS) mode. To implement SPS, thus eliminating the sample matrix, a packed column in the flow cell was used; the chosen sorbent was Nitrilotriacetic Acid Superflow resin (NTA). The possibility of performing an analytical curve resorting to just one standard was also demonstrated. The consumption of the hexadentante ligand was about 30 μg per determination and the effluent production lower than 2.5 mL. The dynamic concentration range was 0.45–9.0 μmol L^{-1}, with a limit of detection of 0.13 μmol L^{-1} and limit of quantification 0.43 μmol L^{-1}. The proposed μSI-LOV-SPS methodology was successfully applied to river, ground, estuarine, tap, and sea waters.

1. Introduction

Iron is introduced in the ocean by dust deposition and the concentration of iron in seawater is expected to be in the order of nanomol L^{-1}, thus being difficult to quantify [1]; additionally, sea water is a high complex matrix due to abundance of other analytes such as magnesium, calcium and chloride. Due to its relevancy, as part of oceanic biogeochemistry and biological activity, there is the need to exploit new analytical techniques with low detection limits [2]. One of the challenges of targeting iron quantification in sea waters is the potential interferences from the matrix, namely high salinity. Atomic absorption spectrometry (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) display good selectivity and sensitivity but they have low tolerance for high salt content. Furthermore, these techniques do not allow in-situ analysis, and require expensive instrumentation and consumables. Alternatively, molecular spectrophotometric techniques can be used for iron quantification in environmental samples, potentially allowing in situ determination and analyte speciation. Another advantage of molecular spectrophotometric detection is its potential for easy coupling with flow analysis techniques [3]. Several features result from this combination like achieving lower reagent

consumption and effluent production, multi-parametric determinations, and automation. Flow techniques comprises relatively inexpensive components, including low-cost miniaturized detectors, thus allowing the efficient implementation of methods for water analysis [4].

However, the colour-forming reactions used in molecular spectrophotometry may involve toxic chromogenic reagents. In this context, use of iron chelators based on 3-hydroxy-4-pyridinone was recently described [5–8] aiming at a greener approach for iron determination. In most of the reported work, bidentate ligands were used [5–7] but one exploited the use of a hexadentate 3-hydroxy-4-pyridinone chelator (CP256) and proved to be the best choice (higher sensitivity) [8]. This chelator, CP256, a tripodal hydroxypyridinone was a specially designed hexadentate ligand with high affinity for complexing iron(III) (log β = 34.4) [9] and with a 1:1 stoichiometry.

The experience in working with these ligands proved the significant advantage in using micro sequential injection lab-on-valve technique (μSI-LOV) [6] over conventional sequential injection analysis [5]. The use of μSI-LOV enables a step further in miniaturization with consequent minimization of reagent and sample consumption. Moreover, the μSI-LOV technique permits to accommodate a sorbent material at the flow cell and potentially to perform the measurement directly at the

---

solid material [10] (solid phase spectrometry). This feature was also previously exploited with the bidentate ligands, using NTA Superflow resin for iron(III) retention [6]. The choice of this resin was based on its necessary transparency [10] and selective retention of iron (III) at a pH ≈ 2 [1,11,12].

In this work, a µSI-LOV method with solid phase spectrophotometry (SPS) for the iron(III) quantification with a specially designed hexadentate 3-hydroxy-4-pyridinone chelator (CP256) is proposed. The idea is to retain iron(III) in the NTA resin placed in the flow cell and to discard the water matrix towards waste. Then, if the CP256 ligand is perfused through the solid material, the coloured complex can be measured directly at the cell, and elute the iron(III) from the resin. In this way, the solid material can be used for several measurement cycles.

In order to minimize the number of solutions prepared and the amount consumed in the analytical process, a single standard strategy to obtain the analytical curve was also implemented. This consists in using a single standard solution, and loading different amounts of iron (III) into the column, by varying the volume of standard sent to the sorbent material.

2. Experimental

2.1. Reagents and solutions

All the solutions were prepared with analytical grade chemicals and Milli-Q water (MQW) resistivity > 18.2 MΩ cm (Millipore, USA).

The hexadentate 3,4-hydroxypyridinone ligand (CP256) solution was obtained by dissolving approximately 10 mg of the synthesized ligand in 20.0 mL of MQW, corresponding to a concentration of $0.5 \, g \, L^{-1}$ ($521 \, \mu mol \, L^{-1}$). The ligand had been previously synthesized and characterized [9] and the denotation of CP256 was adopted from that work.

The $0.60 \, mol \, L^{-1}$ carbonate buffer, pH 10.6, was prepared by dissolving 2.52 g of sodium hydrogen carbonate (Merck, Germany) in 50.0 mL of water and the pH adjusted to 10.6 with 2.5 M sodium hydroxide.

The $0.5 \, mol \, L^{-1}$ nitric acid was prepared from dilution of the concentrated acid ($d = 1.4$; 65%, Merck).

The $180 \, \mu mol \, L^{-1}$ iron(III) stock solution was obtained by dilution of the commercial standard of $18.0 \, mmol \, L^{-1}$ ($1001 \, mg \, L^{-1}$ Fluka - Sigma-Aldrich, Switzerland). This solution was used to prepare an $18.0 \, \mu mol \, L^{-1}$ iron(III) intermediate solution to weekly prepare the Fe^{3+} working standards in the $0.45–9.0 \, \mu mol \, L^{-1}$ range, with $0.03 \, mol \, L^{-1}$ nitric acid.

The chelating resin was Nitrilotriacetic Acid (NTA) Superflow resin (Qiagen, Netherlands), highly cross-linked 6% agarose, 60–160 µm of bead diameter, 50% suspension in 30% ethanol. To load the resin into the flow cell, a 1:3 (v/v) dilution was made to ensure a < 10% ethanol concentration. The NTA resin was packed daily and washed with nitric acid (pH ≈ 2) after each cycle. A working day could include about 4 analytical curves, corresponding to about 60 cycles.

2.2. Sequential injection manifold and procedure

The micro sequential injection lab-on-valve solid phase spectrometry (µSI-LOV-SPS) method developed is outlined in Fig. 1. It consisted of a FIAlab – 3500 (FIAlab Instruments, USA) comprising a bidirectional syringe pump of 2.5 mL and a lab-on-valve head mounted on the top of a six-port selection valve. The detection system comprised a USB 2000 Ocean Optics (USA) CCD spectrophotometer, fiber optics cables (FIA-P200-SR, 400 mm) and a Mikropack DH-2000-BAL deuterium halogen light source. For flow programming and data acquisition, FIAlab for Windows 5.0 software on a personal computer (HP Compaq) was used. The bead column was attained by packing the NTA resin between the two optical fibers with a 10 mm optical path (Fig. 1B). To prevent resin losses, a PTFE stopper (aligned with the

central channel) and a PEEK tube, with inner diameter of 0.06 mm (1560, Nat 1/16 × .0025 × 5 ft, Upchurch Scientific, USA), were used.

For the connection of the different components of the flow system, tubes of polytetrafluoroethylene (PTFE) with 0.8 mm inner diameter were used, including a 1.5 m holding coil.

Operating procedures of the developed flow system for iron(III) determination with the respective volumes used is shown in Table 1.

The syringe pump was filled with carrier prior to the aspiration of standard solutions (step A and B), then standard was propelled towards the flow cell through the NTA column (step C) for iron(III) retention. For attaining an analytical curve, different volumes of the same standard were used, resulting in different retained amounts. The volume propelled was 1.5 times larger than the volume of the standard solution to ensure a complete washing of the column. Afterwards, the CP256 ligand and buffer solutions were sequentially aspirated (steps D and E) and a reference scan was made (step F) before propelling the solutions through the NTA resin, to ensure similar detection conditions. The reference scan enabled to minimize the effect of the beads movement when propelling sample/standards solutions. Then, the ligand and buffer were sent through the column (step G) for the coloured complex formation, allowing both the absorbance measurement, and iron(III) removal from the NTA resin.

After the measurement, nitric acid was aspirated and propelled through the NTA resin to prepare it for the next cycle by appropriate reconditioning (steps H and I).

2.3. Sample collection and preparation

The natural waters, including river, ground, estuarine, tap, and sea waters used, were collected in polyethylene plastic bottles of 0.5 L capacity and acidified (pH < 2) at the collection according to the reference standard procedure [13].

2.4. Accuracy assessment

Three certified water samples were analysed with the developed µSI-LOV method and the result compared with the certified values: NRC-CNR SLRS-4 (river water) from National Research Council, Canada, SPS-SW2 (sea surface water) from National Institute of Standards and Technology (USA) and NIST 1640 (spring water) from National Institute of Standards and Technology.

Additionally, a ground water and a tap water were analysed by atomic absorption spectrometry (APHA 3111B) [13], and the results also compared to those obtained with the developed µSI-LOV method.

3. Results and discussion

The developed work aimed to quantify iron(III) in various types of natural waters, including sea waters, using solid phase extraction of iron(III) prior to the determination to eliminate potential matrix interferences. The idea was to use solid phase spectrometry, made possible by the optical transparency of the NTA resin [14], together with the capacity of the hexadentate ligand (CP256) to remove iron(III) from the NTA by forming a coloured complex (maximum absorption at 460 nm) [8]. Several parameters were set according to previous studies, namely the use of carbonate buffer, pH 10.6, solution ($0.6 \, mol \, L^{-1}$) to ensure the appropriate reaction pH (pH ≈ 7) [8] and the minimal reproducible amount of 5 µL for buffer volume [8,15]. In a previous work, an attempt was made to use both the ligand with the buffer in a single solution. However, the reagent solution prepared this way was not stable; an increase of the solution colour was observed, meaning that it had to be prepared daily [6]. To minimize the influence of the schlieren effect [16], the analytical signal corresponded to subtracting the absorbance measured at 800 nm from the one at 460 nm.
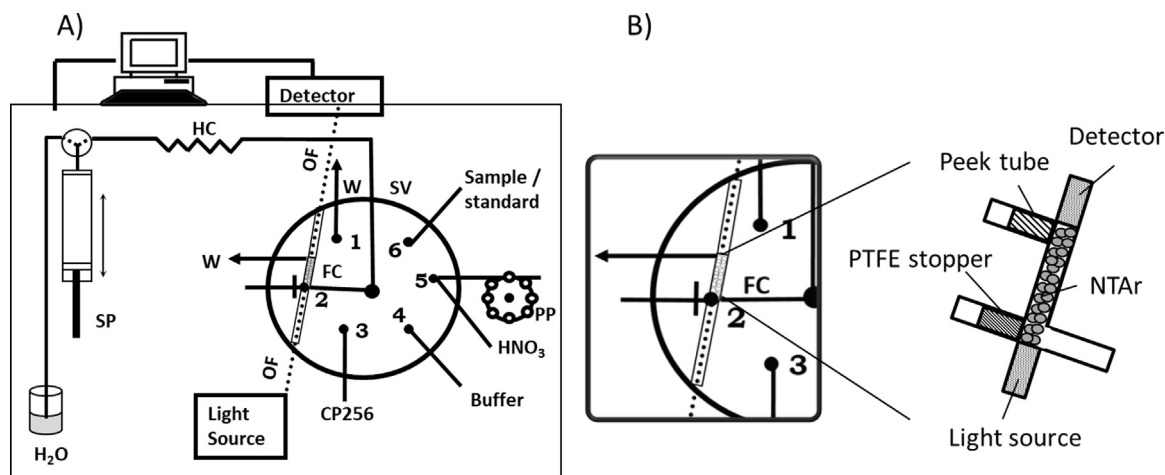
Fig. 1. The micro sequential injection lab-on-valve solid phase spectrometry (µSI-LOV-SPS) manifold: **A)** SV, 6 port selection valve; SP, 2.5 mL syringe pump; HC, 150 cm holding coil; FC, flow cell with NTA resin with 10 mm optical path; OF, optical fibers; W, waste; CP256, 0.5 g L^{-1} hexadentate 3,4-hydroxypyridinone solution; Buffer, 0.6 mol L^{-1} carbonate buffer, pH 10.6; HNO$_3$, 0.5 mol L^{-1}; **B)** flow cell detail, scheme of NTA resin packed between the two optical fibers.

Table 1
Operation procedure of the developed µSI-LOV-SPS method for iron(III) determination using a single standard.

Step	Valve position	Flow rate (µL s^{-1})	Volume (µL)	Description
A	–	200	970–1300[a]	Filling the syringe with carrier
B	6	100	40–700[a]	Aspiration of standard
C	2	10	60–1050[a]	Propelling to detector through the NTA resin
D	3	80	60	Aspiration of hexadentate ligand
E	4	10	5	Aspiration of buffer
F	–	–	–	Reference scan
G	2	10	515	Propelling to detector, absorbance measurement, and iron(III) removal from NTA resin
H	5	100	250	Aspiration of nitric acid
I	2	10	750	Propelling through the NTA resin for washing /conditioning

[a] values used for samples.

3.1. Solid phase spectrometry study

3.1.1. Resin column - NTA resin

As mentioned above, NTA superflow resin was packed in the flow cell to attain matrix elimination prior to colour-forming reaction. The first study was to assess the efficiency of retaining iron(III) in NTA resin at pH ≈ 2. For this study, two analytical curves were set by using standards in the range 0.90–9.0 µmol L^{-1}, with and without the use of NTA, using the same volumes of ligand solution (60 µL) and standard solution (700 µL) and the same optical pathlength (1 cm).

The analytical curve with NTA (A$_{NTA}$ = 0.0446 ± 0.0039 × [Fe^{3+}] + 0.029 ± 0.014) represented over a 15-fold increase in sensitivity when compared to the analytical curve obtained without the NTA (A = 0.00285 ± 0.00007 × [Fe^{3+}] + 0.0004 ± 0.0003). Furthermore, with NTA, it was possible to increase the dynamic concentration range, starting from 0.45 µmol L^{-1}.

The results indicate that the iron(III) was efficiently retained in NTA at pH ≈ 2 and that the hexadentate ligand CP256 effectively eventually removed it.

3.1.2. Column breakthrough

The column breakthrough corresponds to the maximum amount of iron(III) that can be retained in the column of sorbent material. This was assessed by using an iron(III) standard of 9 µmol L^{-1} and successively increasing different volumes of this solution, therefore loading different mass values into the packed NTA resin. The absorbance values increased significantly (> 14%) up to 6.27 nmol (0.35 µg) of iron(III) and then started to stabilize (< 7% increase); so, that amount was considered as the maximum amount retained in the 10 mm NTA resin column (ESI Fig. 1). As this value corresponded to the highest value of

the analytical curve, some problems could arise in working close to the column breakthrough. To minimize potential problems, a washing step after propelling the sample and prior to the colour-forming reaction was studied; the washing volume was set to 1.5 times the sample volume.

3.2. Study of physical-chemical parameters for the complex formation

3.2.1. Sample volume

The sample volume was set to 700 µL as higher volumes would result in working above the maximum NTA column breakthrough.

3.2.2. Hexadentate ligand solution (CP256)

The concentration of CP256 ligand, 0.5 g L^{-1}, was adopted from the previous work [8], so the following study was to assess the influence of the volume of ligand. From the tested range of 40–70 µL, a volume of 60 µL was chosen as it corresponded to the highest sensitivity (analytical curve slope) as it is shown in Fig. 2.

3.3. Calibration with a single standard

Exploiting the feature of retaining the analyte and discarding the matrix, a one standard approach was tested. The idea was to use only a single standard and passing different volumes through the NTA, resulting in different amounts retained and eluted with the same reagent volume, thus resulting in an analytical curve. If successful, this strategy would have the advantage of preparing only a single standard solution, producing less waste volume, and improve the analytical curve rate. The 9 µmol L^{-1} iron(III) standard was used to achieve a calibration range from 0.45 to 9.0 µmol L^{-1}, like the analytical curve with multiple standards, and the two analytical curves were compared (Table 2). For
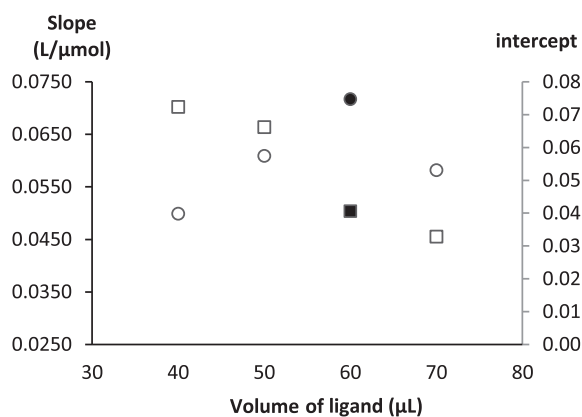
Fig. 2. Study of the influence of CP256 ligand solution volume on the analytical curve slope (○) and intercept (□); the points in black represent the chosen volume.

the multiple standards analytical curve, 700 μL of each standard solution (step B in Table 1) was aspirated and propelled through the NTA resin.

There was no difference between the two approaches in the method sensitivity (slope relative deviation ≈ 3%). However, as expected, there was a significant improvement in time saving, over 30 min, and in effluent volume produced, 30% decrease. So, the analytical curve made with only a single standard, and loading different volumes, was the approach chosen. The LOD and LOQ were calculated for each approach from the analytical curve intercept [17], and the results showed no significant differences (the relative deviations < 8%).

3.4. Interference assessment

3.4.1. Salinity

Considering the aim of applying the developed method to seawater samples, potential salinity interference in the determination was investigated. Iron standards were prepared in both MQW water and in synthetic seawater [18] and the established analytical curves compared. The estimated slopes of the analytical curves were evaluated at 95% confidence intervals, and there was no statistical difference (relative deviation < 3%).

3.4.2. Other ions

In order to evaluate the potential interference of other cations in the reaction or NTA retention, an interference study was carried out for several bivalent and trivalent cations. For this study, several standards were prepared having the same iron(III) concentration (2.7 μmol L^{-1}), and with different ratios of potential interfering metal ion (Me). The interference percentage was calculated as relative deviation between the signals obtained, with ($A_{Fe\&Me}$) and without (A_{Fe}) the potential interfering ion $[(A_{Fe\&Me} - A_{Fe}) \div A_{Fe}]$. The tested ions, the maximum ratio without interference, the minimal interfering ratio and the respective percentages are presented in Table 3.

In the case of cadmium and lead, the ratio 1:0.008, corresponding to

Table 3
Assessment of the influence of potential interfering ions (Me) with the developed μSI-LOV-SPS method, using an iron standard of 2.7 μmol L^{-1}; values in bold represent the maximum ratio with no significant interference.

Potential interfering ion (Me)	Molar ratio Iron: Me (1: x)	% interference
Al^{3+}	**9**	**4%**
	35	−11%
Ca^{2+}	**14**	**−1%**
	28	−13%
Co^{2+}	**1**	**−5%**
	2	−8%
Cu^{2+}	**1**	**0.3%**
	6	−13%
Mg^{2+}	**77**	**−3%**
	345	9%
Mn^{2+}	**2**	**0%**
	14	−15%
Ni^{2+}	**32**	**2%**
	48	19%
Zn^{2+}	**4**	**2%**
	11	10%
NO$_3^-$	**75**	**2%**
	300	−26%
Cd^{2+}	**0.007**	**3%**
	0.008	24%
Pb^{2+}	**0.005**	**2%**
	0.007	29%

a concentration of these cations over 100 times lower than the iron(III) concentration, results in a significant interference (> 20%). However, that would correspond to concentration of Cd and Pb of about 27 nmol L^{-1}, which is not expected in natural waters.

As for the ions with relative high content in seawaters, namely magnesium, up to a concentration 300 times higher than the iron(III) concentration produced no significant interference (≈ 9%), a key feature for seawater application.

3.5. Analytical characteristics

The characteristics of the developed μSI-LOV-SPS method for iron (III) determination based on the colour-forming reaction with CP256 ligand were summarized in Table 4.

The limits of detection and quantification, LOD and LOQ, were calculated according to IUPAC recommendations [17], i.e as the concentration calculated from a signal of either three (LOD) or ten (LOQ) times the mean of the intercept for four analytical curves.

The repeatability of the method was assessed by calculating the relative standard deviation (RSD) of a water sample. The analysis frequency was calculated for the entire analytical curve due to the single standard approach, and for an individual sample. To perform one analytical curve with five concentration values in triplicates 15 analytical cycles, with different times for each concentration, are needed. As for an individual sample in triplicate only 3 analytical cycles (without time variation) are needed. An analytical cycle is the sum of the time needed for each step plus the time necessary for the port selection in the selection valve. The same approach was used to calculate the effluent

Table 2
Comparison between the analytical curves obtained from a single standard and multiple standards within 0.45 – 9.0 μmol L^{-1} dynamic range.

Procedure	Analytical curve[a] A = S x μmol L^{-1} Fe + b	Time for an analytical curve (h)	Effluent volume (mL)
Single standard	A = 0.0483 ± 0.0011 × [Fe^{3+}] + 0.003 ± 0.001 R^2 = 0.9995 ± 0.0004	0.95	25
Multiple Standards	A = 0.0467 ± 0.0039 × [Fe^{3+}] + 0.023 ± 0.014 R^2 = 0.9998 ± 0.0008	1.6	35

[a] n = 4.

as minimizing flow dispersion. The pre-concentration and matrix discarding has proved essential for attaining the required dynamic ranges for natural waters application [6,8,20,21].

Furthermore, the SPS approach, with the NTA resin placed at the detector and the colour-forming reaction being carried out in the resin surface, permitted the use of single standard solution approach, reducing the number of standard solutions needed and decreasing even further analysis time and effluent production.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.talanta.2018.08.063.

References

[1] A. Spolaor, P. Vallelonga, J. Gabrieli, G. Cozzi, C. Boutron, C. Barbante, Determination of Fe^{2+} and Fe^{3+} species by FIA-CRC-ICP-MS in Antarctic ice samples, J. Anal. At. Spectrom. 27 (2012) 310–317.

[2] E.P. Achterberg, T.W. Holland, A.R. Bowie, R.F.C. Mantoura, P.J. Worsfold, Determination of iron in seawater, Anal. Chim. Acta 442 (2001) 1–14.

[3] P.J. Worsfold, M.C. Lohan, S.J. Ussher, A.R. Bowie, Determination of dissolved iron in seawater: a historical review, Mar. Chem. 166 (2014) 25–35.

[4] R.B.R. Mesquita, A.O.S.S. Rangel, A review on sequential injection methods for water analysis, Anal. Chim. Acta 648 (2009) 7–22.

[5] R.B.R. Mesquita, R. Suárez, V. Cerdà, M. Rangel, A.O.S.S. Rangel, Exploiting the use of 3,4-HPO ligands as nontoxic reagents for the determination of iron in natural waters with a sequential injection approach, Talanta 108 (2013) 38–45.

[6] R. Suárez, R.B.R. Mesquita, M. Rangel, V. Cerdà, A.O.S.S. Rangel, Iron speciation by microsequential injection solid phase spectrometry using 3-hydroxy-1(H)-2-methyl-4-pyridinone as chromogenic reagent, Talanta 133 (2015) 15–20.

[7] R.B.R. Mesquita, T. Moniz, J.L.A. Miranda, V. Gomes, A.M.N. Silva, J.E. Rodriguez-Borges, A.O.S.S. Rangel, M. Rangel, Synthesis and characterization of a 3-hydroxy-4-pyridinone chelator functionalized with a polyethylene glycol (PEG) chain aimed at sequential injection determination of iron in natural waters, Polyhedron 101 (2015) 171–178.

[8] J.L.A. Miranda, R.B.R. Mesquita, A. Nunes, M. Rangel, A.O.S.S. Rangel, Iron speciation in natural waters by sequential injection analysis with a hexadentate 3-hydroxy-4-pyridinone chelator as chromogenic agent, Talanta 148 (2016) 633–640.

[9] A. Nunes, M. Podinovskaia, A. Leite, P. Gameiro, T. Zhou, Y. Ma, X. Kong, U.E. Schaible, R.C. Hider, M. Rangel, Fluorescent 3-hydroxy-4-pyridinone hexadentate iron chelators: intracellular distribution and the relevance to anti-mycobacterial properties, J. Biol. Inorg. Chem. 15 (2010) 861–877.

[10] J. Ruzicka, Lab-on-valve: universal microflow analyzer based on sequential and bead injection, Analyst 125 (2000) 1053–1060.

[11] M.C. Lohan, A.M. Aguilar-Islas, R.P. Franks, K.W. Bruland, Determination of iron and copper in seawater at pH 1.7 with a new commercially available chelating resin, NTA Superflow, Anal. Chim. Acta 530 (2005) 121–129.

[12] J. Jong, V. Schoemann, D. Lannuzel, J. Tison, N. Mattielli, High-accuracy determination of iron in seawater by isotope dilution multiple collector inductively coupled plasma mass spectrometry (ID-MC-ICP-MS) using nitrilotriacetic acid chelating resin for pre-concentration and matrix separation, Anal. Chim. Acta 623 (2008) 126–139.

[13] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, 3500 Fe B: Standard Methods for the Examination of Water and Waste Water, 20th ed, American Public Health Association, Washington, DC, 1998, pp. 3.76–3.78.

[14] I.C. Santos, R.B.R. Mesquita, A.O.S.S. Rangel, Micro solid phase spectrophotometry in a sequential injection lab-on-valve platform for cadmium, zinc, and copper determination in freshwaters, Anal. Chim. Acta 891 (2015) 171–178.

[15] A. González, R.B.R. Mesquita, J. Avivar, T. Moniz, M. Rangel, V. Cerdà, A.O.S.S. Rangel, Microsequential injection lab-on-valve system for the spectrophotometric bi-parametric determination of iron and copper in natural waters, Talanta 167 (2017) 703–708.

[16] E.A.G. Zagatto, M.A.Z. Arruda, A. 0 Jacintho, I.L. Mattos, Compensation of the Schlieren effect in flow-injection analysis by using dual-wavelength spectrophotometry, Anal. Chim. Acta 234 (1990) 153–160.

[17] L.A. Currie, Nomenclature in evaluation of analytical methods including detection and quantification capabilities (IUPAC Recommendations 1995), Pure Appl. Chem. 67 (1995) 1699–1723.

[18] D.R. Kester, I.W. Duedall, D.N. Connors, R.M. Pytkowicz, Preparation of artificial seawater, Limnol. Oceanogr. 12 (1) (1967) 176–178.

[19] D.T. Burns, K. Danzer, A. Townshend, Use of the terms "recovery" and "apparent recovery" in analytical procedures, Pure Appl. Chem. 74 (11) (2002) 2201–2205.

[20] S. Ohno, N. Teshima, T. Sakai, K. Grudpan, M. Polasek, Sequential injection lab-on-valve simultaneous spectrophotometric determination of trace amounts of copper and iron, Talanta 68 (2006) 527–534.

[21] B. Horstkotte, P. Chocholouš, P. Solich, Large volume preconcentration and determination of nanomolar concentrations of iron in seawater using a renewable cellulose 8-hydroquinoline sorbent microcolumn and universal approach of post-column eluate utilization in a lab-on-valve system, Talanta 150 (2016) 213–223.