

# Multivariate optimization for cloud point extraction and determination of lanthanides†

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A cloud point extraction (CPE) method is proposed for pre-concentration of lanthanides and subsequent determination using inductively coupled plasma optical emission spectrometry (ICP OES). Octylphenoxypolyethoxyethanol (Triton X-114) and 1-(2-thenoyl)-3,3,3-trifluoroacetone (TTA) are used as surfactant and complexant of the lanthanides, respectively. A three-factor Doehlert matrix design with seven, five, and three levels is used to optimize the TTA and Triton X-114 concentration and the pH of the solution, respectively. The better conditions for pre-concentration are 0.001 to 0.005 mol L<sup>-1</sup> TTA, 0.05 to 0.3% (m/v) Triton X-114 and pH from 5.5 to 7.0. Under these conditions, the fourteen naturally occurring lanthanide elements can be pre-concentrated together and then measured. The conditions established were pH 6.0 and 0.175 (m/v) Triton X-114 for all investigated elements; 0.005 mol L<sup>-1</sup> TTA for Sm, Eu, Gd, Tb, Ho, Yb and Lu; and 0.001 mol L<sup>-1</sup> TTA for La, Ce, Pr, Nd, Dy, Er and Tm. By using axially viewed plasma and pneumatic nebulization/aerosol desolvation, the limits of detection were 0.028, 0.099, 0.103, 0.020, 0.018, 0.014, 0.013, 0.047, 0.015, 0.009, 0.022, 0.003, 0.002 and 0.002 µg L<sup>-1</sup> for La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu, respectively. The proposed method was applied for lanthanides determination in mineral water, river water and reference water.

## 1. Introduction

The lanthanide elements have been increasingly used in a number of applications (as catalysts for different purposes,<sup>1</sup> in batteries,<sup>2</sup> lasers and luminescent materials<sup>1</sup>). They have also been used as tracers in biomolecules studies and as contrast agents in noninvasive diagnosis.<sup>3</sup> The use and demand for lanthanides tend to increase even more in view of their wide range of applications. As a consequence, more lanthanides are entering into the environment, demanding monitoring of these elements.

Inductively coupled plasma optical emission spectrometry (ICP OES)<sup>4–7</sup> and inductively coupled plasma mass spectrometry (ICP-MS)<sup>8–10</sup> are the techniques most employed for lanthanides determination. However, the limit of detection (LOD) of ICP OES may not be compatible for the determination of very low concentrations, requiring a pre-concentration step.<sup>11</sup> Cloud point extraction (CPE) has been investigated for matrix separation and pre-concentration of different elements,<sup>12,13</sup> including the lanthanides.<sup>14,15</sup> The CPE method is based on micelles production by surfactant and subsequent separation<sup>16</sup> in aqueous solutions. Once the critical micellar concentration (CMC) is achieved, the micelles are separated by increasing the

temperature or adding a salting-out agent. The separated micelles constitute a surfactant-rich phase whose volume is low (usually in the range of 50 to 250 µL).

Metals and metalloids react with complexants and produce hydrophobic complexes that are entrapped into the micelles and then into the surfactant-rich phase.<sup>17</sup> In the case of lanthanides extraction/pre-concentration, 8-hydroquinolein and octylphenoxypolyethoxyethanol (Triton X-114) have been employed as complexant and surfactant, respectively.<sup>14,15</sup> Due to the viscosity and organic content of the surfactant-rich phase, which affect plasma performance and stability, appropriate sample introduction systems and nebulizers are required, such as employment of a free-clogging nebulizer,<sup>18</sup> chemical vapour generation,<sup>17</sup> and micronebulization/aerosol desolvation.<sup>19</sup> Analysis of very low amount of solution is possible by using micronebulization/aerosol desolvation.<sup>20,21</sup> Furthermore, aerosol desolvation promotes better sample transport efficiency to the ICP and better sensitivity as a consequence. This system is appropriate for introduction of small volumes of the surfactant-rich phase into the ICP.

The development of a method based on CPE requires the evaluation and optimization of several parameters.<sup>17</sup> Univariate optimization may be a time-consuming and labor-intensive procedure, requiring several experiments. On the other hand, the number of experiments needed is lower in multivariate optimization,<sup>22–24</sup> reducing costs and waste generation. By using this approach, more information is obtained about the interaction

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among the variables, which may be undetected in the case of using univariate optimization. Therefore, a multivariate approach represents a better way to perform the optimization of the variables, thus conducting a more thorough investigation of the method than the common univariate procedure. Doehlert matrix designs can be used for multivariate optimization, involving two, three, or more factors (variables). An important property of the Doehlert design concerns the free choice of the factors to be assigned to a larger or a smaller number of levels, allowing the identification of critical points at each step of the optimization process.

In the present study, Doehlert matrix design is proposed for multivariate optimization and development of a method of lanthanides pre-concentration and determination using CPE and ICP OES, respectively. A micronebulization/aerosol desolvation system is used for introducing the surfactant-rich phase into the ICP. Triton X-114 is used as a surfactant while 1-(2-thenoyl)-3,3,3-trifluoroacetone (2-TTA – Fig. 1S†) is used for lanthanides pre-concentration. This reagent has already been employed for pre-concentration of other elements (Cd, Co, Cr, Cu, Fe and Mn)<sup>25</sup> and Cr speciation<sup>26</sup> using CPE, but not for lanthanides.

## 2. Experimental part

### 2.1 Instrumentation

An Optima 2000 DV ICP OES spectrometer (from PerkinElmer, Shelton, USA) was employed for lanthanides determination. Argon from White Martins/Praxair (Brazil) was used as plasma gas and auxiliary gas, whereas nitrogen with a purity of 99.996% (from White Martins/Praxair) was used as the purging gas. The following ionic spectral lines (wavelength in nm) were monitored: La-398.852; Ce-413.380; Pr-414.311; Nd-406.109; Sm-360.949; Eu-381.967; Gd-335.047; Tb-350.917; Dy-353.170; Ho-345.600; Er-349.910; Tm-313.126; Yb-328.937 and Lu-261.542. These spectral lines were selected as reported elsewhere.<sup>27</sup> A high efficiency nebulizer ESI APEX-Q (ESI, Omaha, NE) was used for sample introduction into the ICP. The sample was introduced through a PFA microconcentric nebulizer fitted to a cyclonic spray chamber heated at 140 °C. The aerosol was then transported to a Peltier-cooled multipass condenser where the temperature was –3 °C. The instrumental conditions used are summarized in Table 1.

A pH meter, a water bath with temperature control and a centrifuge were used to measure the pH of the solutions, as a source of heating (to assist CPE) and for separation of the surfactant-rich phase, respectively. A Doehlert design (Doehlert

1.0) developed at Laboratório de Quimiometria Teórica e Aplicada of UNICAMP/Brazil<sup>28</sup> and MATLAB 7.0 (used for obtaining the response surfaces) were used in chemometric analysis.

### 2.2 Reagents and solutions

Nitric acid 65% (in mass), methanol and ethanol (all from Merck, Darmstadt, Germany) were used. The nitric acid was further purified by sub-boiling distillation (a DuoPor-Milestone system was used). High-purity water (resistivity of 18.2 MΩ cm) obtained from a Milli-Q system (Millipore Corp., USA) was used for preparation of all samples and solutions. Triton X-114 from Sigma (USA) was used for CPE. A 10% m/v Triton X-114 stock solution was prepared by weighing 5.00 g of the reagent in a polypropylene vial and making up to 50 mL with water. The stock solution of Triton X-114 was prepared this way due to the difficulty in measuring an exact volume of the viscous reagent. A 0.1 mol L<sup>-1</sup> TTA (Sigma-Aldrich) stock solution, used for the lanthanides complexation, was prepared by dissolving 0.222 g of the reagent in 10 mL of ethanol. The pH of all samples and calibration solutions was adjusted with ammonium acetate buffer solution (pH = 6.86). The calibration solutions were prepared by serial dilution of 1000 mg L<sup>-1</sup> mono-element stock solutions of the lanthanides (Ultra Scientific from USA). The lanthanides concentration in calibration solutions ranged from 2.0 to 12 µg L<sup>-1</sup> (in 0.7 mol L<sup>-1</sup> HNO<sub>3</sub> for direct lanthanides determination) or 0.5 to 5 µg L<sup>-1</sup> (in ammonium acetate buffer for lanthanides solution submitted to CPE).

### 2.3 Samples and sample preparation

Mineral water (purchased in a local market), river water (from Rio dos Sinos, RS, Brazil) and reference water (SPS-SW1 from Spectrapure Standards AS, Oslo, Norway) were analyzed. Rio dos Sinos receives a variety of effluents from agricultural areas and could be contaminated with lanthanide elements. The river water sample was collected in a cleaned polyethylene bottle and then filtered by means of Whatman filter paper for fast filtration before being submitted to CPE.

Aliquots of 7 mL of sample solution or calibration solution were transferred to graduated polypropylene vials. Next, 350 or 770 µL of 0.1 mol L<sup>-1</sup> TTA and 0.245 g of 10% (m/v) Triton X-114 solutions were added and the volume of the mixture was made up to 14 mL by adding buffer solution to obtain pH = 6.0. For multivariate optimization, different aliquots of TTA, Triton X-114 and buffer solutions were added to obtain the planned concentrations and pH shown in Table 2. The TTA and Triton X-114 concentration and pH were chosen as further discussed in the text. The mixture was heated in a water bath (at 60 °C for 20 min) in order to accelerate the separation of the phases, centrifuged at 3200 rpm for 5 min and then cooled in an ice bath for 10 min. The temperature and time of incubation were used according to previous works.<sup>19,25</sup> The aqueous phase obtained after CPE was removed by inversion of the vial and the surfactant-rich phase was subsequently taken by using a Pasteur pipette. The final volume of the surfactant-rich phase was 150 µL. Subsequently, 100 µL of methanol + 1.0 mL of 0.1 mol L<sup>-1</sup> HNO<sub>3</sub> were added to the surfactant-rich phase and

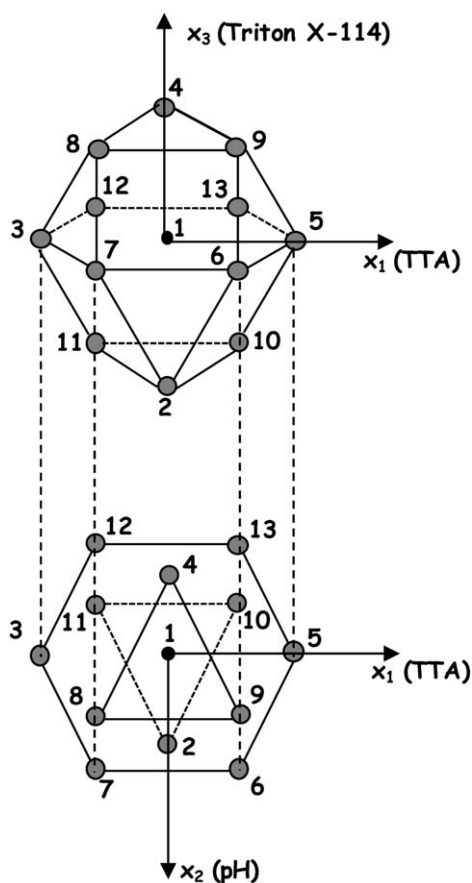
**Table 1** Instrumental and ICP OES parameters

RF power/W	1300
Observation height/mm	15
Plasma gas flow rate/L min <sup>-1</sup>	15
Auxiliary gas flow rate/L min <sup>-1</sup>	0.20
Nebulizer carrier gas flow rate/L min <sup>-1</sup>	0.60
Nebulizer	APEX-Q
Sample flow rate/mL min <sup>-1</sup>	0.65
Plasma view mode	Axial
Resolution	High
Background correction	2 points per peak
Signal processing	Peak area (7 points per peak)

**Table 2** Experimental design and planned values for three variables ( $X_1$ ,  $X_2$  and  $X_3$ )

Experiment	Experimental design			Planned values		
	$X_1$	$X_2$	$X_3$	TTA/ mol L <sup>-1</sup>	pH	Triton/ % (m/v)
1	1	0	0	0.0053	7.0	0.175
2	0.5	0.866	0	0.0094	6.0	0.175
3	0.5	0.289	0.817	0.0066	6.0	0.277
4	-1	0	0	0.0053	3.0	0.175
5	-0.5	-0.866	0	0.0011	4.0	0.175
6	-0.5	-0.289	-0.817	0.0039	4.0	0.073
7	0.5	-0.866	0	0.0011	6.0	0.175
8	0.5	-0.289	-0.817	0.0039	6.0	0.073
9	-0.5	0.866	0	0.0094	4.0	0.175
10	0	0.577	-0.817	0.0080	5.0	0.073
11	-0.5	0.289	0.817	0.0066	4.0	0.277
12	0	-0.577	0.817	0.0025	5.0	0.277
13	0	0	0	0.0053	5.0	0.175
14	0	0	0	0.0053	5.0	0.175
15	0	0	0	0.0053	5.0	0.175

the obtained solution was introduced into the ICP by using the nebulization/aerosol desolvation system. The volume of Triton X-114 and methanol was as low as possible to avoid the dilution



**Fig. 1** Illustration of Doehlert design<sup>30</sup> with 13 points and two extra points (corresponding to replicates of the central point in position 1). Experimental variables: TTA concentration ( $X_1$ ), pH ( $X_2$ ) and Triton X-114 concentration ( $X_3$ ).

of the surfactant-rich phase and plasma loading with methanol, respectively. The calibration solutions were submitted to the same treatment given to samples. For analyte recovery tests, aliquots of the samples were spiked with the lanthanides before being submitted to CPE.

## 2.4 Experimental design

In a Doehlert design, the number of experiments ( $N$ ) is defined by the equation  $N = k^2 + k + 1$ , where  $k$  is the number of factors (variables) involved in the study.<sup>29</sup> The optimal conditions for CPE were evaluated using a three-level factorial design with a central point involving the variables. The variables were TTA and Triton X-114 concentrations and pH, which were studied at seven, five and three levels, respectively. The coded values of the factor levels for the three variables are shown in Table 2. Preliminary tests revealed that lanthanides complex with TTA in solution with pH in the range of 3.0 to 7.0 and in the presence of Triton X-114 whose concentration in the solution is at least 0.05% (m/v). For concentrations of Triton X-114 higher than 0.3% (m/v) a memory effect was observed. It was also observed that the amount of TTA required was very low. Therefore, these three variables were chosen for multivariate optimization.

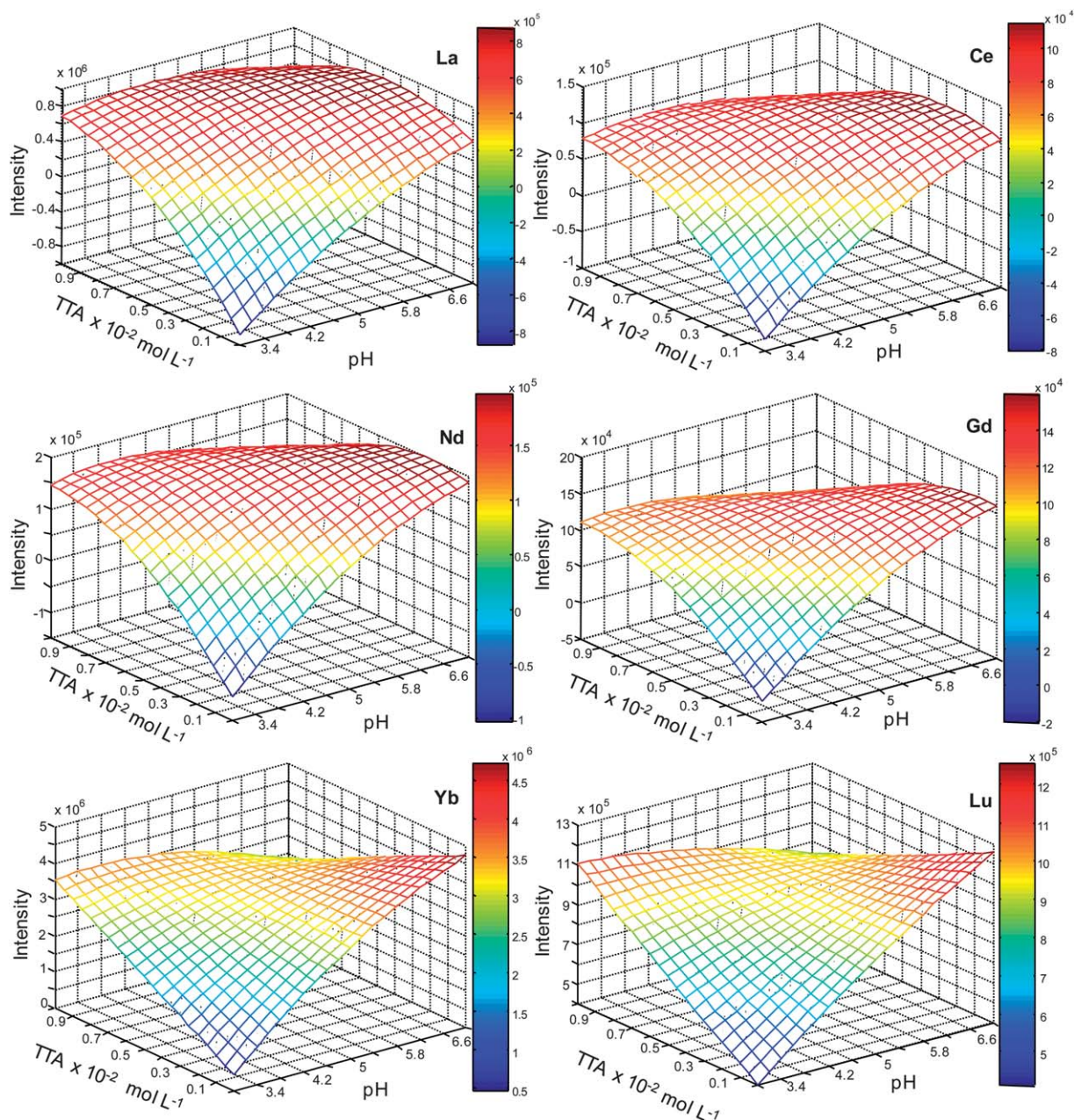
The number of experiments that were carried out was 15; one replicate of each central point (Fig. 1) in addition to the 13 different experiments required by the three-factor design. Each experiment was repeated three times to perform a statistical analysis.

## 3. Results and discussion

The first step of a multivariate optimization process consists in the choice of the most influent responses and factors. In the present study, three variables were considered most important; the TTA concentration ( $X_1$ ), pH ( $X_2$ ) and Triton X-114 concentration ( $X_3$ ). The domain of each variable was chosen according to preliminary results and the experiments were then planned in order to homogeneously cover the experimental domain. In the case of three-variable designs, a cube-octahedron is formed geometrically.<sup>30</sup> The 13 combinations of the parameters evaluated are schematized in Fig. 1; one variable was studied at seven levels (from 0.0005 to 0.01 mol L<sup>-1</sup>, corresponding to the TTA concentration), the second at five levels (from 3.0 to 7.0, corresponding to pH) while the third was studied at three levels (from 0.05 to 0.3% m/v, corresponding to the Triton X-114 concentration).

Response surfaces were obtained by three dimensional plots of two variables (TTA concentration and pH). The Triton X-114 concentration was kept constant (0.175% m/v) because it revealed low influence in the range evaluated.

Fig. 2 and 2S (ESI†) show the response surfaces obtained, indicating that the analyte signal is higher for pH ranging from 5.5 to 7.0. The optimal conditions shown by the surface response are those denoted by the more dark red colour (see the scale on the right of figures). The optimal concentration of TTA is not similar for all investigated elements. For La, Ce, Nd, Pr, Dy, Er and Tm, the highest signals are observed for 0.0050 mol L<sup>-1</sup> TTA (this concentration represents the central point obtained in the



**Fig. 2** Response surfaces obtained for La, Ce, Nd, Gd, Yb and Lu in solution submitted to CPE. Response surfaces for the other lanthanides are shown in Fig. 2S in the ESI.†

response surface), while for Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb and Lu the highest signal is observed for  $0.0011 \text{ mol L}^{-1}$  TTA.

All lanthanides form stable trivalent cations, whose radius decreases with increasing atomic number (lanthanide contraction phenomenon). Thus, the ionic (the same applies to the neutral lanthanide atoms) radius of La is greater than that of Lu. As a result, the coordination number of lanthanides also varies. The observed differences with respect to TTA concentration may be due to ionic radius and basicity variation along the lanthanide series, which is related to the electronic distribution and shielding by *f* orbitals. In Fig. 2 one can note the different response surfaces of Yb and Lu, where the 4*f* orbital is almost completely filled (4*f*<sup>13</sup> for Yb) or filled (4*f*<sup>14</sup> for Lu). However, the optimal

condition with respect to the concentration of TTA is the same as that for Sm, Eu, Gd, Tb, Ho, Er, Tm, Yb and Lu.

The conditions established following the Doehlert optimization for lanthanides pre-concentration using CPE are summarized in Table 3.

### 3.1 Figures of merit and results

The figures of merit of the proposed method for lanthanides pre-concentration using TTA are summarized in Table 3. The detection limits (LODs) were calculated using  $b + 3s$ ; *b* is the average concentration of 10 consecutive measurements of the analyte in the blank (also submitted to CPE) and *s* is the standard



**Table 3** Conditions and figures of merit of the method developed for lanthanides pre-concentration using cloud point extraction (CPE) prior to detection using ICP OES; LOD (limit of detection) in  $\mu\text{g L}^{-1}$ . The concentration of Triton X-114 was 0.117%

Element	pH	TTA/ $\text{mol L}^{-1}$	LOD present method	EF	LOD ICP-MS <sup>20</sup>	LOD ICP OES <sup>14</sup>
La	6.0	0.0053	0.028	14	0.004	0.182
Ce	6.0	0.0053	0.099	10	0.004	0.099
Pr	6.0	0.0053	0.103	14	0.003	0.247
Nd	6.0	0.0053	0.020	11	0.018	0.448
Dy	6.0	0.0053	0.015	10	0.011	0.114
Er	6.0	0.0053	0.022	9	0.012	0.088
Tm	6.0	0.0053	0.003	10	0.003	0.078
Sm	6.0	0.0011	0.018	10	0.016	0.264
Eu	6.0	0.0011	0.014	9	0.011	0.066
Gd	6.0	0.0011	0.013	12	0.013	0.448
Tb	6.0	0.0011	0.047	9	0.004	0.286
Ho	6.0	0.0011	0.009	9	0.004	0.114
Yb	6.0	0.0011	0.002	11	0.010	0.041
Lu	6.0	0.0011	0.002	12	0.003	0.078

deviation. The LODs obtained (between 0.002 and 0.100  $\mu\text{g L}^{-1}$ ) are lower than those found (from 0.041 to 0.448  $\mu\text{g L}^{-1}$  – Table 3) for lanthanides<sup>14</sup> by using 8-hydroxyquinoline (8-Ox) as a chelating agent, CPE and ICP OES for analyte pre-concentration and detection, respectively. The lower LODs obtained in this work can be attributed not only to the multivariate optimization and complexant used, but also to aerosol desolvation that improves sensitivity. It can be observed in Table 3 that the LODs obtained are similar to those found by using ICP-MS, excepting La, Ce, Pr and Tb. In the case of Yb, the LOD obtained is even smaller of that for ICP-MS (aerosol desolvation was also employed for lanthanides quantification using ICP-MS).

The enrichment factors (EFs) found in the present work are in the range of 9 to 14 (Table 3). They were calculated by the ratio of the slopes of the calibration curves obtained for the lanthanides in solution submitted or not to CPE. The correlation coefficient of the calibration curves (not shown in Table 3) was typically 0.996 to 0.999. The proposed method was applied for lanthanides determination in mineral water and river water samples. Despite the low LODs, the lanthanides were not

detected in the analyzed samples. Reference water and analyte recovery tests were carried out to evaluate the performance of the method. The results are presented in Table 4 where one can see that good recoveries were obtained (between 88 and 108%).

The major difficulty to analyze digested samples is the need for pH adjustment, since it must be in the range between 3.0 and 7.0. According to multivariate optimization, the best range of pH is between 5.5 and 7.0, as shown in Fig. 2 and 2S (ESI†). Complexation among TTA and lanthanides does not occur if the pH of the solution is less than 3.0, whereas there is precipitate production if pH is higher than 7.0. The proposed method was applied to pre-concentration of lanthanides in a solution of digested tea, but it was not possible to obtain quantitative results. It was concluded that additional studies are necessary for lanthanides determination in samples different from those analyzed in the present work.

#### 4. Conclusions

A method for lanthanides pre-concentration and determination was developed using Doehlert design, cloud point extraction and ICP OES. Multivariate optimization revealed the best conditions for pre-concentration of all naturally occurring lanthanides. By using TTA as the chelating agent, Triton X-114 as the surfactant, and aerosol desolvation, satisfactory enrichment factors and low limits of detection were obtained, demonstrating that the method can be used for lanthanides concentration monitoring in fresh water. The main advantages are low reagent consumption and low waste generation. The proposed method is an alternative to those based on the use of solid phase extraction<sup>31</sup> for lanthanides pre-concentration in fresh water.

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**Table 4** Lanthanides concentration found in reference water SPS-W1, spiked river water and mineral water; lanthanides were not detected in river water and mineral water. Concentrations are the average and standard deviation of three determinations ( $n = 3$ )

Element	Mineral water			River water			SPS-SW1		
	Spiked/ $\mu\text{g L}^{-1}$	Found/ $\mu\text{g L}^{-1}$	Recovery/%	Added/ $\mu\text{g L}^{-1}$	Found/ $\mu\text{g L}^{-1}$	Recovery/%	Reference/ $\mu\text{g L}^{-1}$	Found, $\mu\text{g L}^{-1}$	Recovery/%
La	1.00	0.98 ± 0.01	99	1.00	0.94 ± 0.01	94	0.50 ± 0.01	0.49 ± 0.01	98
Ce	1.00	0.93 ± 0.01	93	1.00	0.93 ± 0.08	93	0.50 ± 0.01	0.47 ± 0.01	94
Pr	1.00	0.92 ± 0.03	93	1.00	0.94 ± 0.03	95	0.50 ± 0.01	0.46 ± 0.01	92
Nd	1.00	0.96 ± 0.04	96	1.00	1.01 ± 0.01	101	0.50 ± 0.01	0.49 ± 0.02	98
Dy	0.50	0.45 ± 0.01	90	0.50	0.49 ± 0.01	98	0.50 ± 0.01	0.52 ± 0.03	104
Er	0.50	0.44 ± 0.01	88	0.50	0.47 ± 0.02	94	0.50 ± 0.01	0.53 ± 0.02	106
Tm	0.50	0.46 ± 0.01	93	0.50	0.48 ± 0.01	96	0.50 ± 0.01	0.51 ± 0.02	102
Sm	0.50	0.46 ± 0.01	93	0.50	0.47 ± 0.01	95	0.50 ± 0.01	0.48 ± 0.02	96
Eu	0.50	0.46 ± 0.01	93	0.50	0.49 ± 0.01	99	0.50 ± 0.01	0.54 ± 0.02	108
Gd	0.50	0.45 ± 0.01	91	0.50	0.48 ± 0.01	97	0.50 ± 0.01	0.51 ± 0.01	102
Tb	0.50	0.46 ± 0.03	92	0.50	0.47 ± 0.01	94	0.50 ± 0.01	0.46 ± 0.01	92
Ho	0.50	0.48 ± 0.01	97	0.50	0.47 ± 0.01	95	0.50 ± 0.01	0.48 ± 0.01	96
Yb	0.50	0.48 ± 0.01	97	0.50	0.47 ± 0.01	96	0.50 ± 0.01	0.47 ± 0.02	94
Lu	0.50	0.50 ± 0.01	100	0.50	0.48 ± 0.01	97	0.50 ± 0.01	0.52 ± 0.02	104

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