

## Multi-Pumping Mechanised Determination of Selenium in Natural Waters by Light Emitting Diode (LED) Spectrometry

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Um procedimento para determinação de selênio em águas, completamente mecanizado, foi desenvolvido empregando um fotômetro baseado em LED e mini-bombas solenóide como dispositivos de propulsão. O método proposto é baseado na reação de selênio com iodeto de potássio em meio ácido para liberar iodo, o qual oxida a variamina azul formando um composto violeta que absorve em 530 nm. O sistema foi mecanizado empregando o processo de multicomutação em fluxo e uma estratégia de parada de fluxo na etapa final para desenvolvimento da reação. A curva analítica foi linear entre as concentrações de 0,010 a 0,500 mg L<sup>-1</sup>, segundo a equação  $\Delta A = 0,501 (\pm 0,004) C$  ( $R = 0,999$ ). O limite de detecção ( $3\sigma/S$ ) obtido com o método proposto foi de 0,004 mg L<sup>-1</sup>. Desvios padrão relativo de 1,6 e 1,8% ( $n = 4$ ) foram obtidos para soluções de Se com concentrações de 0,050 e 0,200 mg L<sup>-1</sup>, respectivamente. A frequência de amostragem foi de 23 determinações por hora, e a exatidão foi de 95% de probabilidade.

It has been developed a fully mechanised procedure for the determination of selenium in waters employing a LED based spectrometer and solenoid multi-pumps as solution propelling devices. The proposed method is based on the reaction of selenium with potassium iodide in an acidic medium to liberate iodine, which oxidizes Variamine Blue to form a violet-colour species which absorb at 530 nm. The system was mechanised using the multicommutation process and a stopped flow strategy in the final step reaction. The analytical curve was linear between 0.010 and 0.500 mg L<sup>-1</sup>, with an equation  $\Delta A = 0.501 (\pm 0.004) C$  and  $r = 0.999$ . The limit of detection ( $3\sigma/S$ ) obtained for the proposed method was 0.004 mg L<sup>-1</sup>. The relative standard deviation for Se solutions of 0.050 and 0.200 mg L<sup>-1</sup> ( $n = 4$ ) were 1.6 and 1.8% respectively, the sampling throughput was 23 determinations *per* hour, and accuracy was 95% probability level.

**Keywords:** selenium, water, multi-pumping, mechanised flow system, LED-photometry, multicommutated flow system

### Introduction

Selenium is reported as a toxic element as well as an essential trace element for animals and humans.<sup>1,2</sup> In terms of sources of selenium in the environment it can be noticed volcanic eruption, insecticides, fertilizers, smelting ceramic, metallurgical operation, glass rubber accelerators, paints, dyes and electronic goods,<sup>3</sup> additionally there are some industrial and agricultural processes which can cause the presence of Se in natural waters.<sup>4</sup> According to the sanitary and hygiene standards, 0.05 mg L<sup>-1</sup> is the maximum permissible concentration of Se in water,<sup>5</sup> and 0.1-0.2 mg dm<sup>-3</sup>

the Threshold Limit Value (TLV) for selenium compounds in air.<sup>6</sup>

Spectrophotometric methods reported in the literature for the determination of Se in water are based on the batch reaction of Se with potassium iodide in an acidic medium to liberate iodine, which oxidizes leuco malachite green,<sup>3</sup> or Variamine Blue<sup>7</sup> to produce a coloured product; oxidation of *p*-nitroaniline by selenium (IV) followed by reaction with N-(1-naphthalene-1-yl)ethane-1,2-diamine dihydrochloride (NEDA)<sup>8</sup> or previous gas extraction of Se followed by reaction with and 2-(*p*-nitrophenyl)-3,5-diphenyltetrazolium chloride.<sup>9</sup>

Kinetic spectrophotometric methods have been also reported based on the reduction of trisodium 4,5-dihydroxi-3-[(*p*-sulfophenyl)]-2,7-naphthalenedisulfonic acid by sulphide in

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micellar media<sup>10</sup> or on acceleration of the oxidation of methyl orange with bromate in acid media after preconcentration of elemental selenium on activated carbon.<sup>11</sup>

A Flow Injection Analysis (FIA) procedure based on the oxidation of 3-methyl-2-benzothiazolinone hydrazone hydrochloride (MBTH) by selenium (IV) followed by reaction with 4,5-dihydroxy naphthalene-2,7-disulphonic acid in basic medium is the single precedent on mechanized procedures for Se determination in waters.<sup>12</sup>

In classical FIA the continuous solution pumping is made by using peristaltic pumps to propel samples and reagents. Nowadays, reagents solutions can be saved and waste reduced by employing flow manifolds based on sequential injection analysis (SIA)<sup>13</sup> or multicommutated flow injection analyses (MCFIA)<sup>14</sup> and multi-pumping approach.<sup>15</sup> In the MCFIA approach, a set of solenoid valves are assembled to work as independent commutation devices requiring an external device to propel solutions. In the multi-pumping approach the flow systems comprised a set of solenoid micro-pumps, controlled by computer to deliver samples of solution of constant volume.<sup>15</sup> In these systems, different flow rates should be easily achieved by varying the on/off switching pattern of the micro-pumps using a similar electronic hardware to that usually employed in multicommutation. This characteristic facilitates the construction of set-ups with small dimensions suitable for *in situ* use.

Micro-pumps flow systems have been used for determination of anionic surfactants in water<sup>16</sup> and associated with pinch solenoid valves for the determination of paracetamol in pharmaceuticals.<sup>17</sup>

In this work a micro-pumping flow system was developed using a Light Emitting Diode LED based photometer and a home-made flow cell with an optical path-length of 100 mm for the determination of selenium in water. The method is based on the reaction of selenium with potassium iodide to liberate iodine, and the oxidation of Variamine Blue to form a violet-coloured species. Despite, the aim of the present work has been the improvement of the sensitivity, reagent consumption and throughput of photometric determination by using a low cost instrumental set-up, as compared with classical batch and FIA procedures. Finally and having in consideration the efforts in the last years to develop sustainable procedures, the proposed procedure can then be considered as a clean alternative for selenium determination in waters.<sup>18,19</sup>

## Experimental

### *Reagents and samples*

All solutions were prepared with analytical-grade chemicals and with deionised water (18.2 M $\Omega$  cm)

obtained from a Milli-Q system from Millipore (Molsheim, France).

A 1000 mg L<sup>-1</sup> selenium standard was prepared for selenium dioxide Scharlau Chemie (Barcelona, Spain) in nitric acid 0.5 mol L<sup>-1</sup>. A 0.05% (m/v) 4-amino-4'-methoxy-diphenylamine hydrochloride solution of the solid product from Sigma (Steinheim, Germany) was prepared dissolving 50 mg in 25 mL of 99.8% (v/v) methanol from Scharlau Chemie, and making the volume to 100 mL with deionised water. This solution was prepared daily. 2.5 mol L<sup>-1</sup> hydrochloric acid and 1 mol L<sup>-1</sup> sodium acetate solutions were prepared by dilution of the appropriate amount of Scharlau Chemie reagents in deionised water. A 2% (m/v) potassium iodide solution in deionised water was prepared with KI Merck (Darmstadt, Germany).

For Hydride Generation Atomic Fluorescence Spectrometry (HG-AFS), a 4 mol L<sup>-1</sup> hydrochloric acid, a 12% (m/v) sodium borohydride solution from Fluka (Buchs, Switzerland) and 0.1 mol L<sup>-1</sup> sodium hydroxide solution Scharlau Chemie were prepared in deionised water.

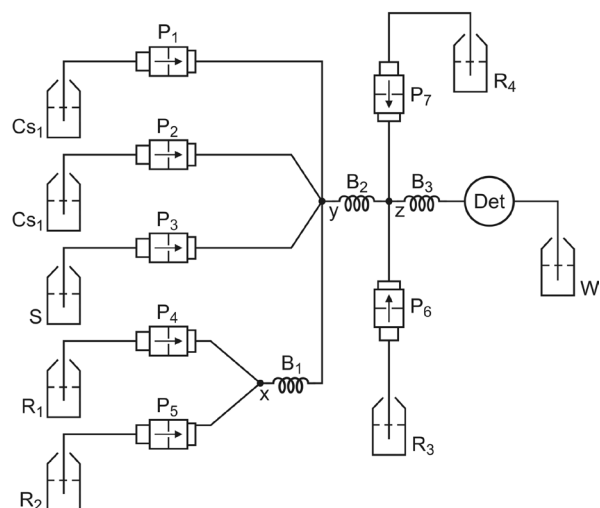
Potential interferents, such as Cl<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup>, Al<sup>3+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Fe<sup>3+</sup> and Cu<sup>2+</sup> were evaluated for solutions containing 0.3 mg L<sup>-1</sup> Se plus the investigated substance at different levels.

Natural water samples were filtered through 0.45  $\mu$ m cellulose membrane filters and stored inside polyethylene bottles before their analysis.<sup>20</sup>

### *Apparatus*

The flow system showed in Figure 1 comprised seven solenoid micro-pumps, from Bio-Chem Valve, 090SP (Boonton, USA); a microcomputer equipped with an electronic interface card Advantech, PCL-711S (San Jose, CA, USA); a homemade electronic interface to drive the micro-pumps similar to that described elsewhere;<sup>21</sup> a homemade LED-based photometer,<sup>22</sup> equipped with a flow cell with 100 mm optical path-length and 2.0 mm inner diameter and a LED with an emission wavelength of 530 nm; reaction coils and flow lines made of PTFE tubing (0.8 mm i.d.) and home-made confluence connectors.

Six micro-pumps (P2 to P7) deliver 8  $\mu$ L solutions *per* pulse. Therefore, the volume of sample and reagent solutions inserted into the analytical path can be controlled by varying the number of the on/off switching cycles. Additionally, to clean the flow system, a 50  $\mu$ L pulse<sup>-1</sup> micro-pump (P1) was employed. The switching frequency was settled at 5 Hz. The flow system control and data acquisition were performed by the microcomputer running software written in Quick BASIC 4.5.



**Figure 1.** Diagram of the flow system. S, sample or standard solution; Cs<sub>1</sub> and Cs<sub>2</sub> carrier fluid, H<sub>2</sub>O; R<sub>1</sub>, 2.5 mol L<sup>-1</sup> hydrochloric acid solution; R<sub>2</sub>, 2% (m/v) potassium iodide solution; R<sub>3</sub>, 1 mol L<sup>-1</sup> sodium acetate solution; R<sub>4</sub>, 0.05% (m/v) 4-amino-4'-methoxy-diphenylamine hydrochloride solution; P<sub>1</sub>, solenoid micro-pump, 50  $\mu$ L pulse<sup>-1</sup>; P<sub>2</sub>, P<sub>3</sub>, P<sub>4</sub>, P<sub>5</sub>, P<sub>6</sub> and P<sub>7</sub> solenoid pumps, 8  $\mu$ L pulse<sup>-1</sup>; B<sub>1</sub>, B<sub>2</sub> and B<sub>3</sub> reaction coils, 120, 190 and 270 cm length respectively, 0.8 mm i.d. PTFE tubing; x, y and z connection devices. Det, LED-photometer,  $\lambda = 530$  nm; W, waste.

### Recommended procedure

The flow set up shown in Figure 1 was designed to be operated following in the time switching micro-pump diagram indicated in Table 1.

After a prior step for filling the mixture coil B1 with hydrochloric acid (R1) and potassium iodide (R2) solutions, which was done by the sequential switching on/off of micro-pumps P4 and P5, the analytical cycle starts as indicated in Table 1.

For the operating conditions shown in Table 1, 20 sampling cycles were programmed to introduce samples and reagents solutions into the analytical path. The micro-pump P6 was switched on/off in all pulses, establishing the baseline,

whereas micro-pumps P3, P4 and P5 were switched on/off sequentially. Thus, for each measurement, a total of 0.64 mL sample or standard were employed (corresponding to 20 cycles of 4 pulse of micro-pump P3) and, at the same time, a total of 0.16 mL of 2.5 mol L<sup>-1</sup> hydrochloric acid solution and 0.16 mL potassium iodide solution (corresponding to 20 cycles of 1 pulse of micro-pumps P4 and P5, respectively).

Samples or standards were mixed together with HCl and KI solutions and accommodated into B2 reactor (190 cm) and the flow stopped for 45 s in order to obtain a satisfactory development of the reaction between potassium iodide and Se(IV).

After reaction development, the micro-pumps P2, P6 and P7 were activated sequentially to do the introduction of R3 and R4. Thirty cycles were used with 4, 2 and 1 pulses of P2, P6 and P7 respectively, in each cycle. Considering that micro-pump P6 introduces 1.0 mol L<sup>-1</sup> sodium acetate solution and that P7 introduces 0.05% 4-amino-4'-methoxy-diphenylamine hydrochloride (VB) solution, the volumes employed of each reagent were, respectively, 0.48 and 0.24 mL. In this step the reaction between VB and I<sub>2</sub> was made into the B3 reactor (270 cm). After the end of fixed cycles, micro-pump P1 (50  $\mu$ L) was activated for pushing the coloured product zone towards the detector and to clean the system after each measurement.

The absorbance data obtained for samples were interpolated in a external calibration line achieved by introduction of different standards of Se(IV) under the same conditions as those used for samples.

## Results and Discussion

### Effect of manifold operating conditions

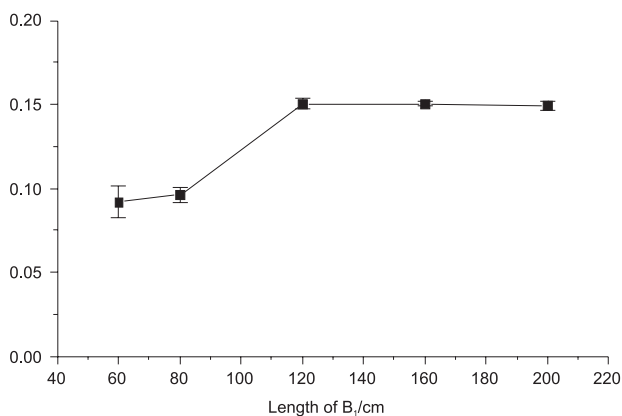
Preliminary experiments were made to establish the B1 mixture coil length. This step was very important to obtain

**Table 1.** Operational conditions of the flow system

Step	Event	P <sub>1</sub>	P <sub>2</sub>	P <sub>3</sub>	P <sub>4</sub>	P <sub>5</sub>	P <sub>6</sub>	P <sub>7</sub>	Pulses	cycles
1	Introduction of S	0	0	on/off	0	0	on/off	0	4	20
	Introduction of R <sub>1</sub>	0	0	0	on/off	0	on/off	0	1	
	Introduction of R <sub>2</sub>	0	0	0	0	on/off	on/off	0	1	
2	Stopped flow (45 s)	0	0	0	0	0	0	0	-	
3	Introduction mixture B <sub>2</sub>	0	on/off	0	0	0	0	0	4	30
	Introduction R <sub>3</sub>	0	0	0	0	0	on/off	0	2	
	Introduction R <sub>4</sub>	0	0	0	0	0	0	on/off	1	
4	Transport to detection cell and cleaning	on/off	0	0	0	0	0	0	300	

Step 1 and 3 inserting of sample and reagent solutions; Step 2, stopped flow of 45 s; Step 4, uses the micro-pump P<sub>1</sub> to transport the reactive mixture and to clean the system after measurement; on/off: input/output solutions into/from micropump. P<sub>1</sub>: 50  $\mu$ L volume micropump; P<sub>2</sub>-P<sub>7</sub>: 8  $\mu$ L volume micropump.

a good mixture between hydrochloric acid and potassium iodide previously to the reaction with Se(IV), specially taking into consideration that this mixture liberates iodine in presence of light, thus it has an effect on the blank signal. Figure 2, shows the effect of B1 length from 60 to 200 cm on the final absorption of the reaction product between iodine and VB generated after reaction of KI with Se(IV). A coil length of 120 cm was chosen, corresponding to an inner volume of 600  $\mu\text{L}$  to obtain the maximum sensitivity. The aforementioned volume was introduced through a sequence of 45 cycles of 1 pulse of micro-pump P4 and 1 pulse of P5.



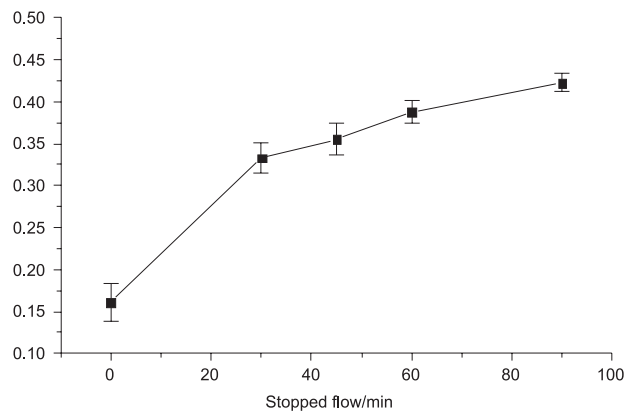
**Figure 2.** Effect of the mixture coil B1 length on absorbance signal. In these experiments the Se concentration was fixed at 1 mg L<sup>-1</sup> being VB concentration 0.05%, KI concentration of 2%, HCl concentration 2 mol L<sup>-1</sup> and sodium acetate 1 mol L<sup>-1</sup>; (n = 4).

Figure 3 shows the effect of the reaction time between KI in HCl and Se(IV). In this study 1 mg L<sup>-1</sup> Se(IV) was mixed with KI and HCl using 10 cycles including 4 pulses of P3, 1 pulse of P4 and 1 pulse of P5. As can be seen, after a stopped flow time of 30 s it can be obtained a sensitivity enhancement of 100%. Additional reaction times increase the analytical signal, but 45 s seems enough to obtain a good compromise between sensitivity and measurement speed.

The oxidation of iodide by selenium occurs at coil B2 and the size of this coil must be adapted to locate the mixture of KI and HCl with the sample or Se standards. 640  $\mu\text{L}$  sample solution 160  $\mu\text{L}$  HCl and 160  $\mu\text{L}$  KI were selected and thus a reaction coil of 190 cm was chosen. So, the length of reaction coil B3 in which I<sub>2</sub> and VB were located was fixed at 270 cm being filled on using 30 cycles of 4 pulses of P2, 2 pulses of P6 and 1 pulse of P7.

#### Effect of reagent concentration

The concentration of hydrochloric acid was varied from 1.5 to 3.0 mol L<sup>-1</sup> and that of sodium acetate from 0.5 to



**Figure 3.** Effect of the reaction time on the stopped flow mode on the signals obtained by the reaction between potassium iodide and Se(IV). In these experiments the Se concentration was fixed at 1 mg L<sup>-1</sup> being VB concentration 0.05%, KI concentration of 2%, HCl concentration 2 mol L<sup>-1</sup> and sodium acetate 1 mol L<sup>-1</sup>. The length of B1 was fixed at 120 cm; (n = 4).

2.0 mol L<sup>-1</sup>. Hydrochloric acid 2.5 mol L<sup>-1</sup> and sodium acetate 1.0 mol L<sup>-1</sup> were selected in order to assure a pH around 1.2 for the first reaction and 4.5 for the second one. For potassium iodide, concentrations below 2% (m/v) limited the analytical sensitivity and concentrations higher than 2% increase the blank values. The concentration of VB was fixed 0.05% (m/v) for all studies.

#### Analytical performance

Table 2 compares the analytical features of the proposed and bibliography procedures. The proposed multicommutation procedure, that use the 100 mm flow injection cell, provides calibration equations of the same order than batch and FIA. The proposed method provides a limit of detection of the same order than that obtained by using NPDPTC after a previous separation of the gas phase generation,<sup>9</sup> and clearly lower than other photometric procedures.<sup>3,7,8</sup> It seems that kinetic spectrophotometric approaches provide an enhancement of the LOD and astonishing the sensitivity reported for FIA spectrophotometric determination with MBTH is one order of magnitude better than that obtained by us. However, on looking through the aforementioned study,<sup>12</sup> it can be seen that authors reported a sensitivity of 0.1875 for the concentration range between 0.050 and 0.500 mg L<sup>-1</sup> which is clearly lower than the value of 0.501 obtained in this study for the range between 0.010 and 0.500 mg L<sup>-1</sup> and thus it is surprising that they could found a LOD of 0.00025 mg L<sup>-1</sup> nor for using a 2 $\sigma$  criterion.

The detection limit (3 $\sigma$ /S) obtained for the proposed method was 0.004 mg L<sup>-1</sup>. The calibration graph, obtained in the range between 0.010 and 0.500 mg L<sup>-1</sup>, provided an equation  $\Delta A = 0.501 (\pm 0.004) C$  with a correlation

**Table 2.** Analytical performance of spectrophotometric methods proposed in bibliography for the determination of selenium in water samples

	Proposed method	Ref. 3	Ref. 7	Ref. 8	Ref. 9 <sup>a</sup>	Ref. 10	Ref. 12
Linear range / (mg L <sup>-1</sup> )	0.01-0.5	0.04-0.4	0.2-2.0	0.02-3.2	0.01-0.12	0.0005-0.1	0.05-0.5
LOD / (µg L <sup>-1</sup> )	4	11	30	17	2	0.0003	0.25 <sup>b</sup>
RSD / (%)	1.58-1.84	0.03-0.07	1.7-2.5	0.8846	-	1.95-2.10	0.2-1.8
Reagents	c	d	c	e	f	g	h
Procedure	multicommutation	batch	batch	batch	batch	kinetic	FIA
Wavelength / nm	530 (LED)	615	546	515	490	515	530
Reagents consumption / mL	2.6	5.0	4.5	3	336	4.2	18
Throughput / h <sup>-1</sup>	23	2.5	-	-	-	-	10

<sup>a</sup>Previous gas extraction of Se; <sup>b</sup>LOD established from 2σ. c: Variamine Blue (VB); d: malachite green; e: N-(1-naphthalene-1-yl)ethane-1,2-diamine dihydrochloride; f: 2-(*p*-nitrophenyl)-3,5-diphenyltetrazolium choride (NPDPTC); g: Trisodium (4,5-Dihydroxi-3-[(*p*-sulfophenyl)]-2,7-naphthalenedisulfonic acid; h: 3-mentyl-2-benzothiazolone hydrazone hydrochloride (MBTH).

coefficient of 0.999. The repeatability was established by the relative standard deviation of 4 measurements at concentrations levels of 0.050 and 0.200 mg L<sup>-1</sup> begin found 1.6 and 1.8% RSD values, respectively. The sampling throughput was of 23 measurements *per* hour.

#### Effect of interfering ions

Natural water is a complex system which can contain several cations and anions, as potential sources of interferences. It was selected thirteen common species usually found in water and results obtained are showed in Table 3. In this study it was fixed a tolerance limit of the interfering species at those concentrations which caused

no more than 5.0% changes in the absorbance peak height of a 0.300 mg L<sup>-1</sup> Se solution.

Table 3 summarizes the limits of the interfering ions evaluated for the determination of Se, being confirmed the excellent selectivity of the method proposed showing a wide tolerance for the assayed chemical species and no severe interfering effect takes place. Besides, taking into account that the maximum acceptable concentration of those species in waters are lower than tolerance limit found, the procedure could be useful for selenium determination in waters.

#### Application

The proposed method was applied for the determination of Se in 9 water, river and bottle mineral samples. All samples presented concentrations of selenium lower than the detection limits of both, the multicommutated proposed method (0.004 mg L<sup>-1</sup>) and the reference HG-AFS procedure (0.009 µg L<sup>-1</sup>). Because of that, samples were spiked at levels between 0.050 and 0.200 mg L<sup>-1</sup> and recovery percentage data are summarised in Table 4. As we can see recoveries varied from 98 to 103%. On the other hand the regression between values found by the recommended procedure (Y) and those obtained by HG-AFS (X) for spiked samples provided a regression equation  $Y = 0.97 (\pm 0.02) X - 0.002 (\pm 0.003)$  with a regression coefficient of 0.996, which clearly shows the good comparability of both approaches and confirming the validity of the multicommutated procedure. Student's paired *t*-test calculated for the values obtained by both procedures was lower than the theoretical *t* value (2.056) for 95% probability level and 26 degree freedom. It can be concluded that the accuracy of the developed procedure is comparable to that found by HG-AFS.

**Table 3.** Study of interferences on the determination of selenium by the developed procedure

Interferent	Reagent	Tolerance limit <sup>a</sup> / (mg L <sup>-1</sup> )	Mass ratio	Molar ratio
Cl <sup>-</sup>	NaCl	3000	10000	22295
CO <sub>3</sub> <sup>2-</sup>	NaHCO <sub>3</sub>	3000	10000	13192
NO <sub>3</sub> <sup>-</sup>	NaNO <sub>3</sub>	2000	6666	8496
SO <sub>4</sub> <sup>2-</sup>	Na <sub>2</sub> SO <sub>4</sub>	2000	6666	54881
PO <sub>4</sub> <sup>3-</sup>	Na <sub>2</sub> PO <sub>4</sub> H	2000	6666	5540
Ca <sup>2+</sup>	Ca(NO <sub>3</sub> ) <sub>2</sub>	2000 <sup>b</sup>	6666	13192
Zn <sup>2+</sup>	Zn(NO <sub>3</sub> ) <sub>2</sub>	400 <sup>b</sup>	1333	1614
Al <sup>3+</sup>	Al(NO <sub>3</sub> ) <sub>3</sub>	400 <sup>b</sup>	1333	3746
Ni <sup>2+</sup>	Ni(NO <sub>3</sub> ) <sub>2</sub>	60 <sup>b</sup>	200	269
Pb <sup>2+</sup>	Pb(NO <sub>3</sub> ) <sub>2</sub>	60 <sup>b</sup>	200	76
Fe <sup>2+</sup>	FeNH <sub>4</sub> (SO <sub>4</sub> ) <sub>2</sub>	10 <sup>b</sup>	33	47
Fe <sup>3+</sup>	Fe(NO <sub>3</sub> ) <sub>3</sub>	10 <sup>b</sup>	33	47
Cu <sup>2+</sup>	Cu(NO <sub>3</sub> ) <sub>2</sub>	10 <sup>b</sup>	33	41

Notes: Studies were made for a fixed concentration of 0.3 mg L<sup>-1</sup> Se(IV).

<sup>a</sup>No interference up to signal variation lower than 5% in presence of the interfering species.

<sup>b</sup>Measurements made in the presence of 3500 mg L<sup>-1</sup> of the EDTA.

**Table 4.** Determination of Se(IV) in spiked water samples

Matrix*	Added / (mg L <sup>-1</sup> )	Found / (mg L <sup>-1</sup> ) <sup>a</sup>	Recovery / %	Mean Value
River water	0.05	0.052 ± 0.003	104 ± 6	103 ± 2
	0.10	0.103 ± 0.003	103 ± 3	
	0.20	0.203 ± 0.002	101 ± 1	
River water	0.05	0.051 ± 0.04	102 ± 8	102 ± 2
	0.10	0.104 ± 0.003	104 ± 3	
	0.20	0.203 ± 0.04	101 ± 2	
Mineral water	0.05	0.049 ± 0.002	98 ± 4	102 ± 4
	0.10	0.105 ± 0.005	105 ± 5	
	0.20	0.200 ± 0.003	104 ± 1	
Mineral water	0.05	0.052 ± 0.001	104 ± 2	101 ± 5
	0.10	0.104 ± 0.001	104 ± 1	
	0.20	0.193 ± 0.002	96 ± 1	
Mineral water	0.05	0.049 ± 0.001	98 ± 2	98 ± 1
	0.10	0.097 ± 0.002	97 ± 2	
	0.20	0.196 ± 0.003	98 ± 1	
Mineral water	0.05	0.049 ± 0.001	98 ± 2	101 ± 2
	0.10	0.102 ± 0.003	102 ± 3	
	0.20	0.205 ± 0.004	102 ± 2	
Mineral water	0.05	0.048 ± 0.002	97 ± 4	100 ± 3
	0.10	0.100 ± 0.001	100 ± 1	
	0.20	0.207 ± 0.002	103 ± 1	
Mineral water	0.05	0.049 ± 0.001	98 ± 2	101 ± 2
	0.10	0.103 ± 0.002	102 ± 2	
	0.20	0.205 ± 0.004	102 ± 2	
Mineral water	0.05	0.048 ± 0.001	96 ± 2	99 ± 3
	0.10	0.102 ± 0.003	102 ± 3	
	0.20	0.201 ± 0.004	100 ± 2	

\*Actual concentrations of Se(IV) in all samples were lower than detection limits obtain by LED photometry (4 µg L<sup>-1</sup>).

<sup>a</sup>Mean ± standard deviation (n = 3).

## Conclusions

The use of micro-pumping multicommutation approach together a home-made LED-photometer with a long path cell enhances the sensitivity of the batch photometric determination of Se seven times and reduces the reagents consume also improving the sampling throughput. The proposed procedure offers a sustainable alternative to the previously proposed methods for selenium determination in water (see Table 2), reducing reagents consumption and waste generation. In front of batch procedures, multicommutation facilitates handling of solutions, minimizes risks for the analyst and provides a more environmental sustainable procedure.

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