Development of a high sensitivity photometric procedure for the determination of vanadium in mineral and fresh waters employing a downsized multicommitted flow analysis approach

Tuanne R. Dias, Jarbas J. R. Rohwedder, Marcos A. S. Brasil and Boaventura F. Reis

This article focuses on the development of an analytical procedure for the photometric determination of vanadium in fresh and mineral waters, implemented employing a downsized multicommitted flow analysis approach. A flow system module using solenoid mini-pumps for fluid propelling and a light emitting diode (LED) based photometer were handled employing a microcontroller (PIC18F). Aiming to improve sensitivity, the flow analysis module and the photometer were designed to allow the coupling of a flow cell with an optical pathlength of 150 mm. The photometric procedure was based on the reaction of V(IV) with eriochrome cyanine R, which formed a compound that presented maximum absorption at 560 nm. Samples of river water and mineral water were processed with the intention to assess the effectiveness of both equipment setup and analytical procedure. The proposed setup presented good overall performance including a linear response (r = 0.997) comprising the concentration range of 0.02 to 1.50 μg mL⁻¹ vanadium; reagent consumption of 11.6 μg eriochrome cyanine R and 8.6 mg ascorbic acid per determination; and a detection limit of 13 µg L⁻¹ vanadium. Other useful features including a relative standard deviation of 0.87% (n = 10), a sampling throughput of 47 determination per hour and a waste generation of 2.4 mL per determination were also achieved.

1. Introduction

The history of vanadium began in 1801, when the chemist Andres Manuel Del Rio presented his idea concerning the existence of a new chemical element, which was discovered in 1830 by the Swedish chemist Nils Sefstrom. Nowadays, vanadium is used in the manufacture of printing inks, pigments, steel, and glass, as well as in the catalyst and ceramic industries. Vanadium occurs in several minerals and fossil compounds including crude oil, coal, oil shale, and tar sands. The industrial use of vanadium as well as burning of fossil fuels are considered to be the main sources of vanadium released into the environment, reaching soil and water supply.

Vanadium at a low concentration is considered to be an essential element for living organisms, participating in biochemical and biological process, contributing to cell growth. Research has indicated that at a low concentration, vanadium presents beneficial effects on human health, including inhibition of cholesterol synthesis. Furthermore, there is an expectation that vanadium possesses cardioprotective properties, including the ability to prevent heart diseases.

According to the references consulted, the beneficial feature of vanadium for human health occurs at a low concentration level, and it becomes toxic at higher concentrations. Vanadium poisoning could cause nervous depression, anemia, vomiting, and so on. Vanadium in aqueous media may occur in the oxidation states from (II) to (V), but the forms V(IV) and V(V) are the most stable. The form V(IV) is considered more toxic than V(V), thereby vanadium has both beneficial and toxic characteristics, while a close relationship is maintained between the essential concentration and levels of toxicity. In this sense, development of analytical procedures for its determination has attracted much interest. Procedures for vanadium determination have been implemented in several types of samples, employing detection techniques such as fluorimetry, spectrophotometry, atomic absorption spectrometry with electrothermal atomization, and optical emission spectrometry with inductively coupled plasma.

Spectrophotometry is a detection technique widely employed for vanadium determination and to improve sensitivity, analytical procedures have been implemented employing pre-concentration steps including solvent extraction, solid phase extraction and solid phase spectrophotometry.
Analytical procedures carried out manually are very time consuming and produce large volumes of waste and as a result, additional work is required to dispose the waste appropriately in order to minimize the impact of the environmental sustainability. Analytical procedures for vanadium determination have also been implemented employing the flow injection analysis (FIA) process, thus allowing throughout improvement. Nevertheless, the continuous pumping of reagent solutions generates a large volume of waste, which is considered as a drawback to be overcome.

Nowadays, the development of miniaturized and portable equipment is considered a trend within the modern analytical chemistry, allowing facilities to accomplish environmentally friendly analytical procedures, which are focused on the reduction of both reagent consumption and waste generation. This trend began in the 1990s, when Manz et al. introduced the concept of Micro Total Analysis Systems (µ-TAS). The authors pointed out that the main reason for miniaturization is the improvement of analytical performance rather than reduction of size. Based on this concept, lab-on-valve and lab-on-chip technologies have been proposed as tools for the downsizing of the flow analysis setup, which has been done using several machining techniques. In some cases, the reduction of dimensions was not so drastic because the radiation source, photodetector and fluid propelling device were not integrated in the sample processing setup. While using the lab-on-chip approach, effective integration was achieved by attaching the radiation source (LED) and the photodetector to the machined chip.

Analyzing those papers, we can observe that saving of reagent and reduction of waste generation were effective, but the sensitivity was not improved, because it was limited by the optical pathlength of the flow cell. According to the Bouguer–Beer–Lambert law, sensitivity can be improved by increasing the optical pathlength, a condition that is very difficult to be attained, while employing a setup based on the lab-on-chip approach. On the other hand, the instrumental setup with a reduced dimension, designed to use a flow cell with a long optical pathlength, allowed an increase in sensitivity while maintaining the µ-TAS guidelines.

These analytical setups based on the multicommuted flow analysis (MCFA) concept consisted of flow analysis modules with solenoid mini-pumps for fluid propelling and LED based photometers furnished with flow cells, which were designed with optical pathlengths ranging from 20 to 100 mm.

In this work, we intend to develop an automated procedure for photometric determination of vanadium in fresh water. Since vanadium concentration may be very low, an equipment setup based on the multicommuted flow analysis approach will be designed to provide high sensitivity while maintaining the µ-TAS guidelines. A flow analysis module based on a multicommuted process can afford facilities to handle small volumes of sample and reagent solutions, which will be exploited in the current work to attain the analytical green chemistry requirements, while maintaining the µ-TAS guidelines.

The flow cell is a component that belongs at the same time to both the photometer and the flow analysis module. Since the optical pathlength of the flow cell presents a direct relationship to sensitivity, the photometer and flow analysis module will be designed to allow the coupling of a flow cell with an optical pathlength ranging from 50 to 150 mm.

The analytical procedure will be developed based on the reaction of vanadium with Eriochrome Cyanine R (ECR), using ascorbic acid solution as a reducing reagent. The compound formed has a maximum absorption of electromagnetic radiation at 560 nm, thus allowing the use of a green LED as the radiation source.

2. Experimental

2.1. Reagents and solutions

All chemicals used were of analytical grade. Purified water presenting electric conductivity less than 0.1 μS cm⁻¹ was used throughout. A 0.05% (m/w) Eriochrome Cyanine R (from Merck) stock solution was prepared by dissolving 0.05 g of solid in 100 mL of water. A 0.007% working solution (25 mL) was prepared before use by dilution with water from the stock solution. An acetate buffer solution 0.35 mol L⁻¹ was prepared by dissolving 28.71 g of sodium acetate (from Merck) in 700 mL of water. After dissolution, the pH was adjusted to 5.0 with glacial acetic acid (from Merck), and the volume was increased to 1000 mL with water. A 0.5% (w/v) ascorbic acid solution was prepared daily by dissolving the solid (from Quimex) in 50 mL of the acetate buffer solution. A 1.0 g L⁻¹ V(V) stock solution was prepared by weighing 0.2296 g of NH₄VO₃ (from Merck) and dissolving it in 1 mL of concentrated HNO₃. After dissolution, the volume was increased to 100 mL with water. Standard solutions of V(V) with concentrations of 0.00, 0.02, 0.04, 0.09, 0.19, 0.38, 0.75, 1.00, 1.50 and 2.00 mg L⁻¹ were prepared daily by dilution with water from a 20 mg L⁻¹ V(V) solution, which was prepared before use from the stock solution.

Intending to verify whether ions usually present in fresh water, such as Al³⁺, Ni²⁺, Pb²⁺, Co²⁺, Mn²⁺, Zn²⁺, Fe³⁺, SO₄²⁻, Cl⁻, F⁻, and NO₃⁻, could cause interference, a set of solutions was prepared containing 1.0 mg L⁻¹ of each potential interfering ion.

River water samples were filtered using a 0.45 μm Millipore filter and acidified by adding 1 mL of concentrated HNO₃ to 1000 mL. Before analysis, aliquots of 25 mL of water were selected, and to them was added a volume of 25 μL of a 1 g L⁻¹ fluoride solution that was prepared using NaF salt. Mineral water was acquired at the local market and before use it was acidified similar to the river samples.

2.2. Apparatus and materials

The flow system module designed to implement the analytical procedure was based on the multicommuted flow analysis process, which was assembled employing one three-way solenoid valve HP225T031 (NResearch), three solenoid mini-pumps PN120SP1210-5TP (Biochem Valve), and two coiled reactors of polyethylene tubing, 20 and 40 cm long and with 0.8
mm inner diameter. These devices were attached to an acrylic platform 20 cm long, 15 cm wide and 1.5 cm thick.

The photometer comprised a 5 mm green LED and a photodiode OPT301 (Burr-Brown). The LED presented a maximum emission at 560 nm and an opening angle of 23°, while the photodetector included together at the same signal transduction unit, the amplification network. Three flow cells with optical pathlengths of 50, 100, and 150 mm and an inner diameter of 1.2 mm, constructed using a borosilicate glass tube, were molded as described in previous work. The supports of the flow cells were tailored in order to allow that assays using the three flow cells were carried out employing the same LED and photodetector. The signal amplification interface, comprising an operational instrumentation amplifier (AD524, Analog Devices) and resistors, that was assembled on a fiberglass plate with dimensions of 5 × 5 cm, which was coupled to the output of the photodiode. The photometer was accommodated into a metallic box (30 cm wide, 15 cm high and 20 cm deep) to protect against external radiation.

A microcontroller PIC18F4550 model manufactured by Microgenios Microcontrollers (São Paulo, Brazil), which possesses digital interfaces, was used to control the flow analysis module, RS 232 and USB serial interfaces, an analog-to-digital converter with 12 bits of resolution, which was configured to work with a full scale of 4096 mV. The microcontroller was configured to work as a slave coupled to a microcomputer through the serial interfaces.

Other equipment and devices comprised a microcomputer furnished with RS 232 and USB serial interfaces, running a software program written in visual Basic 6.0; a regulated power supply (12 V) to feed the mini-pumps and solenoid valve; a regulated power supply (−12 V, +12 V) to feed the photometer; a control digital interface based on the integrated circuit ULN 2803 to drive the mini-pumps and solenoid valve, which was wired as described before; and a transistor BD547 and resistors to assemble the network to control the LED brightening as indicated in Fig. 1. The control interface was coupled to the digital output of the microcontroller PIC18F4550.

2.3. Experimental procedure

Because the reaction to form the compound to be monitored occurred with V(IV), prior to mixing the sample aliquot with chromogenic reagent solution, a reducing step was included in order to convert V(V) to V(IV). Therefore, the flow system module based on the multicommuted approach was designed to fulfill this requirement. The diagram of the integrated system comprising the flow system and the photometer is depicted in Fig. 1.

The control of the flow system and the data acquisition were assisted by a microcomputer running a software program written in Visual Basic 6.0. The microcontroller (PIC18F4550) was configured to work as a slave, communicating with the microcomputer through the serial interface in order to receive the protocol commands to handle the flow system module and to perform data acquisition. The signal generated by the photometer was converted to a digital pattern by the microcontroller and sent to the microcomputer through the serial interface. These data were stored as an ASCII file to allow further treatment. While the analytical run proceeded, a plot of the signal was displayed on the microcomputer screen to allow its visualization at real time.

Initially, the flow system module was in the standby condition, thus no solution was flowing through it. When the software began the analytical run, each mini-pump was switched on/off sequentially 20 times. This action was done to fill each flow line that connects the mini-pumps to the reactors Rc1 and Rc2 with its respective solution. Afterwards, the microcomputer inquired whether photometer calibration would be performed. If calibration was required, the microcomputer instructed the microcontroller to switch the mini-pump P2 on/off 30 times in order to fill the flow cell with the carrier solution (Cs). Afterwards, the signal (Fs) generated by the photometer was read by the microcontroller and sent to the microcomputer. If the Fs value was different from the value established as a reference (Sr = 4000 mV), the microcomputer requested the operator to adjust the signal magnitude Fs to be equal to Sr. This was accomplished by turning the variable resistor coupled to the base of the transistor (Tr, Fig. 1). The residual signal (Rs) related to diffuse radiation was achieved by filling the flow cell with compound solutions, which were obtained by mixing 5 mL of solutions containing 50 and 75 mg L⁻¹ V(n) with equal volumes of a 0.05% m/v ECR solution, producing a very intensely colored solution, which were used to find the residual measurement. If signals achieved while maintaining the flow cell filled with each solution were equal, we should consider that the radiation into the flow cell was completely absorbed by the solutions, thus the residual measurement (Rs) may be attributed to the diffused radiation. The measurements Fs and Rs were saved as references to be used for absorbance calculation.

After the calibration step, the analytical run proceeded following the mini-pump switching pattern depicted in Fig. 1. In the first step (St1), the mini-pump P1 was switched on/off 5 times followed by an on/off switching action applied sequentially to the mini-pumps P2 and P3. This sequence of events as repeated in step St2 is named here as a sampling cycle. The number of sampling cycles can be increased to fill the reactor Rc2 and flow cell with a mixture comprising sample and reagent solutions. The reactions to convert V(n) to V(IV) by ascorbic acid and to form the compound to be detected proceeded while the sample zone was displaced through the reactors Rc1 and Rc2 toward the photometer (Det). The signal generated by the photometer (Si), while steps St1, St2 and St3 proceeded, was read by the microcontroller by means of its analog-to-digital converter and sent to the microcomputer. After absorption calculation, the data were saved as an ASCII file to allow further treatment. While performing the sampling steps (Fig. 1), only the carrier solution (Cs) flowed through the flow cell, so that the signal generated is similar to the reference signal (Sr), thus its record tends to be a straight line that precede signal related to vanadium concentration, which was generated while the reading step (St3) proceeded.

When using a multicommuted flow analysis approach to develop an analytical procedure, the variables that can affect the
overall performance include lengths of reactors, volume of sample zone, time interval for reaction development, reagent concentration, and acidity of the reaction medium. Therefore, assays involving these variables should be implemented in order to select the best working condition. A finalizing these studies and aiming to access the effectiveness of both the proposed setup and the analytical procedure, a set of river and mineral water samples was processed.

### 3. Results and discussion

#### 3.1. Absorbance calculation

The signal (Si) generated by the photodetector was converted to digital and expressed in mV, which was used for absorbance calculation using the equation shown below:

\[
\text{Abs} = \log\left(\frac{\text{Sr} - \text{Rs}}{\text{Si} - \text{Rs}}\right) = kcx
\]

where Sr = reference signal; Rs = residual measurement; Si = signal related to the current measurement; k = constant; c = analyte concentration; x = length of the flow cell.

While performing the calibration step, the Sr value was adjusted to be 4000 mV and the residual measurements (Rs) achieved using flow cells with optical pathlengths of 50, 100, and 150 mm were 64.4, 85.6, and 95.3 mV, respectively. As indicated in the Experimental section, this assay was performed using two solutions with different concentrations. The signals (Rs) generated with each flow cell presented practically equal values, thus indicating that the radiation into the flow cell was completely absorbed. In this sense, the generated signals could be considered as residual measurements. In previous work, it
was demonstrated that when using an LED based photometer, the range of accordance with the Bouguer–Lambert–Beer law was shown to be widened by using the residual measurement for absorbance calculation, therefore this resource was employed in the current work.

3.2. Effect of the sample volume

In a flow analysis system, the volume of the sample and reagent solution plays an important role, because the volume of the sample zone affects the dispersion effect, while the ratio between volumes of sample and reagent solution can affect the stoichiometry of the reaction. In this sense, an appropriate selection of both sample zone volume and volume ratio of sample and reagent solution aliquots is mandatory whether high sensitivity is a focus of the analytical procedures or not. The volume of sample and reagent solution aliquots was the first variable studied, thus to achieve high sensitivity assays were carried out in order to find the better ratio between volumes of sample and reagent solution aliquots. The results indicated that the sample aliquot could be five times the volume of the reagent solution without significant impairment of solution mixing. Therefore, a sampling cycle was established to include 5 strokes of the mini-pump P1 followed by 1 stroke of mini-pumps P2 and P3. Under these conditions, the sample zone formed in the reactor presented a sample volume 5 times higher than the volume of ascorbic acid and erichrome cyanine R solutions. The number of sampling cycles was varied from 3 to 18, thus the volume of the sample zone varied from 210 to 1260 µL. This assay was done using a 0.35 mg L⁻¹ vanadium(V) solution, yielding the results shown in Fig. 2.

Analyzing these curves, we observed that from 15 sampling cycles, the increases in signals were not significant, thus indicating that the volume of the sample zone (1050 µL) was enough to lead the signal generated to a steady state condition. These results show that while volumes of sample zones increased five times, the gain in signals were about four times. Comparing the signals generated using the flow cells with pathlengths of 50 and 150 mm, we can observe that a signal increasing about three-times was achieved. These results show that while increasing the flow cell optical pathlength, the proposed LED based photometer obey the Bouguer–Lambert–Beer law.

It is known that in the flow analysis approach, the length of the reaction coil can play a remarkable role, including solutions mixing as well as time for reaction development, which can be improved by increasing the length of the reaction coil. Nevertheless, this resource causes an increase of sample dispersion that could impair sensitivity. Analyzing the set of curves shown in Fig. 2, we can observe that each one presents an asymptotic behavior for sampling cycles higher than fifteen, whereby indicating that the sample dispersion effect was overcome by increasing the volume of sample zone. In the current work, previous assays implemented by interrupting the pumping of the carrier solution for 15 s, while the signal reading step proceeded, showed that no significant increase in the signal was observed, thus indicating that the length of the reaction coil (40 cm) was enough to allow reaction development.

3.3. Effect of the reagent solution concentration

The results discussed in the previous section were achieved using a 0.007% (w/v) ECR solution. With the intention to find the adequate concentration, experiments were performed varying the ECR solution concentration. Assays were done using a set of vanadium(V) standard solutions with concentrations ranging from 0.04 up to 2.00 mg L⁻¹, yielding the results shown in Table 1. Including results achieved using standard solutions with concentrations higher than 1.50 mg L⁻¹, a decrease in linearity was observed, thus their results were not considered.

The slopes of the linear regression curves represent the sensitivity of the analytical procedure, thus we should consider them as parameters to evaluate the effect of the reagent solution concentration. As we can see, there is a significant increase in sensitivity up to the concentration of 0.007% (w/v), which was also followed by an increase in the intersect value. This effect would be expected, considering that the chromogenic reagent solution also absorbed radiation at 560 nm. Analyzing the results obtained using reagent solution with concentrations of 0.0035 and 0.007, we can observe that while the intersect increased by 43%, the slope increased by only 23%. Furthermore, for higher concentrations an intersect increase of 47% occurred, while no significant increase for slope was observed. Because sensitivity was a goal to be attained, and considering also that increasing the intersect would not impair the linear response range, the ECR concentration of 0.007% was selected.

Table 1  Effect of the reagent concentration

<table>
<thead>
<tr>
<th>Concentration (%)</th>
<th>Concentration range (mg L⁻¹)</th>
<th>Intersect (L mg⁻¹)</th>
<th>Slope (r)</th>
<th>Linear coeff.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0017</td>
<td>0.04–1.50</td>
<td>0.0964</td>
<td>0.1040</td>
<td>0.9975</td>
</tr>
<tr>
<td>0.0035</td>
<td>0.04–1.50</td>
<td>0.1294</td>
<td>0.2321</td>
<td>0.9997</td>
</tr>
<tr>
<td>0.007</td>
<td>0.04–1.50</td>
<td>0.2248</td>
<td>0.3040</td>
<td>0.9997</td>
</tr>
<tr>
<td>0.014</td>
<td>0.04–1.50</td>
<td>0.4217</td>
<td>0.3087</td>
<td>0.9999</td>
</tr>
</tbody>
</table>
Because eriochrome cyanine R reacted with vanadium(IV), an ascorbic acid solution was mixed with sample aliquots in order to cause reduction of vanadium(IV) to vanadium(III). Intending to find adequate solution concentration, assays were done using ascorbic acid solutions with concentrations of 0.25, 0.50 and 1.0% (w/v) and a vanadium(IV) standard solution with a concentration of 1.50 mg L\(^{-1}\). Results show that there was no significant difference between the generated signals, whereby a 0.5% (w/v) ascorbic acid solution was selected.

### 3.4. Effect of the pH

The carrier fluid (Cs) also functioned as a buffer solution, which was accomplished by switching on/off mini-pump P\(_2\) to insert aliquots of Cs solution into the sample zone, as indicated in the sampling step (Fig. 1). The results discussed before were obtained using a carrier solution with pH adjusted to 5.0. Aiming to find the adequate acidity of the reaction medium, a set of assays was implemented using acetic acid buffer solutions with different pH, yielding the results shown in Fig. 3. Analyzing this curve, we observe that the pH of the reaction medium exerts a remarkable effect on the signal up to 5.3, presenting a small decrease for higher pH values, whereby the acetate buffer with a pH of 5.3 was selected.

### 3.5. Figures of merit related to optical pathlength

The focus of the current work was to achieve a high sensitivity analytical procedure, thereby assays were carried out employing flow cells with optical pathlengths of 50, 100, and 150 mm, and their figures of merit are shown in Table 2.

Once the best working conditions were selected, including reagent solution concentration, acidity of reaction medium, and volumes of sample and reagent aliquots, a set of standard solutions was processed employing the flow cell with an optical pathlength of 150 mm and using the parameter values shown in Table 2. These assays were performed in order to access the integrated performance of both setup and analytical procedure.

<table>
<thead>
<tr>
<th>Evaluated parameters</th>
<th>50 mm</th>
<th>100 mm</th>
<th>150 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear range (mg L(^{-1}))</td>
<td>0.04–1.50</td>
<td>0.04–1.50</td>
<td>0.02–1.50</td>
</tr>
<tr>
<td>Linear correlation ((r))</td>
<td>0.998</td>
<td>0.999</td>
<td>0.998</td>
</tr>
<tr>
<td>Limit of detection (µg L(^{-1}))</td>
<td>20</td>
<td>16</td>
<td>13</td>
</tr>
<tr>
<td>Variation coefficient(^a) (%)</td>
<td>0.69</td>
<td>1.58</td>
<td>0.87</td>
</tr>
<tr>
<td>Sampling throughput (h(^{-1}))</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Chromogenic reagent(^b) (µg)</td>
<td>11.6</td>
<td>11.6</td>
<td>11.6</td>
</tr>
<tr>
<td>Ascorbic acid(^b) (mg)</td>
<td>8.6</td>
<td>8.6</td>
<td>8.6</td>
</tr>
<tr>
<td>Sample volume(^b) (µL)</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>Waste generation(^c) (mL)</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
</tbody>
</table>

\(^a\) Consumption and waste generation per determination. \(^b\) Results achieved by performing 10 consecutive measurements using a mineral water sample spiked with 0.38 mg L\(^{-1}\) V(IV).

The parameters to be evaluated included linear response range, limit of detection, and long-term stability. The records of the photometric measurements are shown in Fig. 4.

Taking the maximum value of the records as the measurement parameters, we found the linear graphic (\(r = 0.997\)) shown as an inset of Fig. 4. Aiming to access the limit of detection, the blank solution was subsequently processed 10 times, and the value found, 13 µg L\(^{-1}\), was estimated using the 3\(\sigma\) criterion.\(^44\) Analyzing the records shown in Fig. 4, we can deduce that a sampling throughput of 47 determination per hour would be achieved. Furthermore, we can see that the precision of the measurements as well as uniformity of the record profile are very good, thus indicating a very good long-term stability.

### 3.6. Performance comparison

Comparing the performance of the proposed procedure with those presented by some existing spectrophotometric

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**Fig. 3** Effect of the pH on the signal. Results obtained by processing a vanadium(IV) standard solution with a concentration of 0.35 mg L\(^{-1}\).

**Fig. 4** Record of the measurements. From left records are related to standard vanadium(IV) solutions with concentrations of 0.00, 0.02, 0.04, 0.09, 0.19, 0.38, 0.75 and 1.00 mg L\(^{-1}\).
procedures for determination of vanadium, which are summarized in Table 3, we can observe that the current work affords significant advantages concerning a low volume of waste generation and high sampling throughput. Albeit the limit of detection is higher than those presented in the referred generation and high sampling throughput. Although the detection limit of species, we can observe that only Al<sup>3+</sup> and Fe<sup>3+</sup> caused significant interference. The assays were done employing 1.0 mg L<sup>−1</sup> analytical procedures, a set of assays was accomplished using solutions with these ions. The assays were done employing 1.0 mg L<sup>−1</sup> vanadium(V) standard solutions prepared with and without the potential interfering ions as related in Table 4.

Taking an absorbance variation of ±5% as a criterion for interference and employing the absorbance generated processing a 1.0 mg L<sup>−1</sup> vanadium(V) standard solution as a reference, we can observe that only Al<sup>3+</sup> and Fe<sup>3+</sup> caused significant variation, which would be considered an interference effect. This effect was suppressed by adding sodium fluoride to the assayed solutions, thereby this expedient was also applied for the water samples.

### 3.7. Study of the potential interference

Intending to verify whether ions usually present in fresh water, such as Al<sup>3+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Co<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, Fe<sup>3+</sup>, NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, Cl<sup>−</sup> and F<sup>−</sup>, have any interference effect on the proposed analytical procedures, a set of assays was accomplished using solutions with these ions. The assays were done employing 1.0 mg L<sup>−1</sup> vanadium(V) standard solutions prepared with and without the potential interfering ions as related in Table 4.

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>Concentration (mg L&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Absorbance variation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2−&lt;/sup&gt;</td>
<td>2.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Pb&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Al&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>20</td>
<td>&lt;5*</td>
</tr>
<tr>
<td>Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>300</td>
<td>&lt;5</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;−&lt;/sup&gt;</td>
<td>150</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>2.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;−&lt;/sup&gt;</td>
<td>500</td>
<td>&lt;5</td>
</tr>
<tr>
<td>F&lt;sup&gt;−&lt;/sup&gt;</td>
<td>2.0</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>50</td>
<td>&lt;5*</td>
</tr>
</tbody>
</table>

* Maximum assayed value; * 100 mg L<sup>−1</sup> F<sup>−</sup>.

### 3.8. Determination of vanadium in water samples

Intending to prove the effectiveness of the proposed procedures, samples of river and mineral waters were analyzed. The signal measurements of samples showed that concentrations would be lower than the limit of detection (13 μg L<sup>−1</sup>). The samples were also analyzed employing graphite furnace atomic absorption spectrometry (GF AAS), the results were also lower than the limit of detection (3 μg L<sup>−1</sup>). For this reason, the recovery method was applied in order to allow accuracy assessment, yielding the results shown in Table 5.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added amount (mg L&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Found amount (mg L&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.50</td>
<td>0.462 ± 0.022</td>
<td>92.36</td>
</tr>
<tr>
<td>2</td>
<td>0.50</td>
<td>0.475 ± 0.023</td>
<td>94.94</td>
</tr>
<tr>
<td>3</td>
<td>0.50</td>
<td>0.470 ± 0.014</td>
<td>93.96</td>
</tr>
<tr>
<td>4</td>
<td>0.50</td>
<td>0.440 ± 0.024</td>
<td>87.18</td>
</tr>
<tr>
<td>5</td>
<td>0.50</td>
<td>0.493 ± 0.017</td>
<td>98.62</td>
</tr>
<tr>
<td>Mineral water</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>0.38</td>
<td>0.338 ± 0.001</td>
<td>88.86</td>
</tr>
<tr>
<td>7</td>
<td>0.38</td>
<td>0.349 ± 0.023</td>
<td>91.79</td>
</tr>
<tr>
<td>8</td>
<td>0.38</td>
<td>0.397 ± 0.004</td>
<td>104.52</td>
</tr>
<tr>
<td>9</td>
<td>0.38</td>
<td>0.382 ± 0.027</td>
<td>100.52</td>
</tr>
<tr>
<td>10</td>
<td>0.38</td>
<td>0.416 ± 0.002</td>
<td>109.45</td>
</tr>
</tbody>
</table>

Analyzing these data, we can see that recoveries between 87 and 110% were achieved, which can be considered good.

### 4. Conclusion

The previously discussed results allow us to conclude that the proposed procedure and the instrument setup are reliable and robust. Adequate environmental sustainability according to analytical green chemistry guidelines was achieved by using nontoxic reagents and generating a low volume of waste. The use of an LED based photometer furnished with a flow cell of long optical pathlength is shown to be an effective strategy to
increase sensitivity, allowing improvement in the limit of detection without using laborious pre-concentration steps, resource that has been usually employed.\textsuperscript{7,10,12,17} The proposed setup afforded cost-effective, operational simplicity and as well as a low reagent consumption (11.6 μg of ECR per determination), therefore indicating that it would become a suitable alternative for monitoring of vanadium in samples of environmental interest.

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References
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