

Analytical Methods

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3 Development of a high sensitivity photometric procedure for the determination of
4 vanadium in mineral and fresh waters employing a downsized multicommuted flow
5 analysis approach
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23 This article focuses on the development of an analytical procedure for the
24 photometric determination of vanadium in fresh and mineral waters, implemented
25 employing a downsized multicommuted flow analysis approach. A flow system
26 module using solenoid mini-pumps for fluid propelling and a light emitting diode
27 (LED) based photometer were handled employing a microcontroller (PIC18F).
28 Aiming to improve sensitivity, the flow analysis module and the photometer were
29 designed to allow the coupling of a flow cell with an optical pathlength of 150 mm.
30 The photometric procedure was based on the reaction of V (IV) with eriochrome
31 cyanine R, which formed a compound that presented maximum absorption at 560
32 nm. Samples of river water and mineral water were processed with the intention to
33 assess the effectiveness of both equipment setup and analytical procedure. The
34 proposed setup presented good overall performance including a linear response (r
35 = 0.997) comprising the concentration range of 0.02 to 1.50 $\mu\text{g mL}^{-1}$ vanadium;
36 reagent consumption of 11.6 μg eriochrome cyanine R and 8.6 mg ascorbic acid per
37 determination; and a detection limit of 13 $\mu\text{g L}^{-1}$ vanadium. Other useful features
38 including a relative standard deviation of 0.87% ($n = 10$), a sampling throughput of
39 47 determination per hour and a waste generation of 2.4 mL per determination were
40 also achieved.
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Keywords: Multicommutated flow analysis; Downsized setup; LED based photometer; Flow injection analysis; Vanadium; Fresh water

1. Introduction

The history of vanadium begins 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.¹ Nowadays, vanadium is used in the manufacture of printing inks, pigments, steel, and glass, as well as in the catalyst and ceramic industries.^{2,3,4} Vanadium occurs in several minerals and fossil compounds including crude oil, coal, oil shale, and tar sands.^{5,6} The industrial use of vanadium and 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.^{6,7,8}

Vanadium at a low concentration is considered to be an essential element for living organisms, participating of the biochemical and biological process, contributing to cell growth.^{9,10,11} Research has indicated that at a low concentration, vanadium presents beneficial effects on human health, including inhibition of cholesterol synthesis.^{8,12} Furthermore, there is an expectation that vanadium possesses cardioprotective properties, including the ability to prevent heart diseases.^{8,13,14,15}

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.^{7,8,16,17} Vanadium in aqueous mediums 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(V) is considered more toxic than V(IV)^{2,10,12,18}, 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 aroused much interest. Procedures for vanadium determination have been implemented in several types of samples, employing as detection techniques fluorimetry,¹⁴ spectrophotometry,^{2,7,10,12,17,18,19} atomic absorption spectrometry with electrothermal

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3 atomization,^{20,21} and optical emission spectrometry with inductively coupled
4 plasma.^{22,23}
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7 Spectrophotometry is the detection technique widely employed for vanadium
8 determination and to improve sensitivity, analytical procedures have been
9 implemented employing pre-concentration steps including solvent extraction,^{5,10}
10 solid phase extraction^{7,12} and solid phase spectrophotometry.¹⁶
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13 Analytical procedures carried out manually are very time consuming and
14 produce large volumes of waste^{2,5,7,8,9,12,17,18} and as a result, additional work is
15 required to dispose the waste appropriately in order to minimize the impairment of
16 the environmental sustainability. Analytical procedures for vanadium determination
17 have been also implemented employing flow injection analysis (FIA) process, thus
18 allowing throughput improvement.^{3,10,11,14,16,19} Nevertheless, the continuous
19 pumping of reagent solutions generates a large volume of waste, which is
20 considered as a drawback to be overcome.
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27 Nowadays, the development of miniaturized and portable equipment is
28 considered a trend within the modern analytical chemistry, allowing facilities to
29 accomplish environmentally friendly analytical procedures, which are focused on the
30 reduction of both reagent consumption and waste generation. This trend began in
31 the 1990s, when Manz et al.²⁴ introduced the concept of Micro Total Analysis
32 Systems (μ -TAS). The authors pointed out that the main reason for miniaturization
33 is improvement of analytical performance rather than reduction of size. Based on
34 this concept, lab-on-valve^{25,26,27} and lab-on-chip^{28,29,30,31} technologies have been
35 proposed as tools for the downsizing of the flow analysis setup, which has been
36 done using several machining techniques. In some cases, the reduction of
37 dimension was not so drastic because radiation source, photodetector and fluid
38 propelling device were not integrated in the sample processing setup.^{25,26,27,32} While
39 using the lab-on-chip approach, effective integration was achieved by attaching the
40 radiation source (LED) and the photodetector to the machined chip.^{29,30}
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50 Analyzing those papers, we can observe that saving of reagent and reduction
51 of waste generation were effective, but the sensitivity was not improved, owing to it
52 was limited by the optical pathlength of the flow cell. According to the Bouguer-
53 Beer-Lambert law³³, sensitivity can be improved by increasing the optical
54 pathlength, condition that is very difficult to be attained, while employing setup
55 based on the lab-on-chip approach. On the other hand, instrument setup with a
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3 reduced dimension, designed to use a flow cell with a long optical pathlength,
4 allowed increase in sensitivity while maintaining the μ -TAS guidelines.^{34,35} These
5 analytical setups based on the multicommutated flow analysis (MCFA) concept,
6 consisted of flow analysis modules with solenoid mini-pumps for fluid propelling and
7 LED based photometers furnished with flow cells, which were designed with optical
8 pathlengths ranging from 20 to 100 mm.^{34,35,36}
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11 In this work, we intend to develop an automated procedure for photometric
12 determination of vanadium in fresh water. Since vanadium concentration may be
13 very low, an equipment setup based on the multicommutated flow analysis
14 approach^{36,37} will be designed to provide high sensitivity while maintaining the μ -
15 TAS guidelines. A flow analysis module based on multicommutated process can
16 afford facilities to handle small volumes of sample and reagent solutions,^{38,39} which
17 will be exploited in the current work to attain the analytical green chemistry
18 requirements,^{40,41, 42} while maintaining the μ -TAS guidelines.²⁴
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21 The flow cell is a component that belongs at the same time to both the
22 photometer and the flow analysis module. Since the optical pathlength of the flow
23 cell presents a direct relationship to sensitivity,^{34,35,36} the photometer and flow
24 analysis module will be designed to allow the coupling of a flow cell with an optical
25 pathlength ranging from 50 to 150 mm.
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28 The analytical procedure will be developed based on the reaction of
29 vanadium (IV) with Eriochrome Cyanine R (ECR), using ascorbic acid solution as a
30 reducing reagent. The compound formed has a maximum absorption of
31 electromagnetic radiation at 560 nm,⁴³ thus allowing the use of a green LED as the
32 radiation source.
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35 36 37 38 39 40 41 42 43 44 45 **2. Experimental**

46 47 48 *2.1. Reagents and solutions*

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50 All chemicals used were of analytical grade. Purified water presenting electric
51 conductivity less than $0.1 \mu\text{S cm}^{-1}$ was used throughout. A 0.05% (m/w) Eriochrome
52 Cyanine R (from Merck) stock solution was prepared by dissolving 0.05 g of solid in
53 100 mL of water. A 0.007 % working solution (25 mL) was prepared before use by
54 dilution with water from the stock solution. An acetate buffer solution 0.35 molL^{-1}
55 was prepared by dissolving 28.71 g of sodium acetate (from Merck) in 700 mL of
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3 water. After dissolution, the pH was adjusted to 5.0 with glacial acetic acid (from
4 Merck), and volume was increased to 1000 mL with water. A 0.5% (w/v) ascorbic
5 acid solution was prepared daily by dissolving the solid (from Quimex) in 50 mL of
6 the acetate buffer solution. A 1.0 gL⁻¹ V (V) stock solution was prepared by
7 weighting 0.2296 g of NH₄VO₃ (from Merck) and dissolving it in 1 mL of
8 concentrated HNO₃. After dissolution, the volume was increased to 100 mL with
9 water. Standard solutions of V(V) with concentrations of 0.00, 0.02, 0.04, 0.09,
10 0.19, 0.38, 0.75, 1.00, 1.50 and 2.00 mgL⁻¹ were prepared daily by dilution with
11 water from a 20 mg L⁻¹ V(V) solution, which was prepared before use from the stock
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20 Intending to verify whether ions usually present in fresh water, such as Al³⁺,
21 Ni²⁺, Pb²⁺, Co²⁺, Mn²⁺, Zn²⁺, Fe³⁺, SO₄²⁻, Cl⁻, F⁻, NO₃⁻ could cause interference, a set
22 of solutions was prepared containing 1.0 mg L⁻¹ of V(V) and 0.0, 0.5, 1.0, and 2.0
23 mg L⁻¹ of each potential interfering ions.
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27 River water samples were filtered using a 0.45 μm Millipore filter and acidified
28 by adding 1 ml of concentrated HNO₃ to 1000 mL. Before analysis, aliquots of 25
29 mL of water were selected, and to them was added a volume of 25 μL of a 1 gL⁻¹
30 fluoride solution that was prepared using NaF salt. Mineral water was acquired at
31 the local market and before use was acidified similarly to the river samples.
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37 *2.2. Apparatus and materials*

38 The flow system module designed to implement the analytical procedure was
39 based on the multicommutated flow analysis process,^{34,35,36,37} which was assembled
40 employing one three-way solenoid valve HP225T031 (NRResearch), three solenoid
41 mini-pumps PN120SP1210-5TP (Biochem Valve), and two coiled reactors of
42 polyethylene tubing, 20 and 40 cm long and with 0.8 mm inner diameter. These
43 devices were attached to an acrylic platform 20 cm long, 15 cm wide and 1.5 cm
44 thick.
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50 The photometer comprised a 5 mm green LED a photodiode OPT301 (Burr-
51 Brown). The LED presented a maximum emission at 560 nm and an opening angle
52 of 23°, while the photodetector included together at the same signal transduction
53 unit, the amplification network. Three flow cells with optical pathlengths of 50, 100,
54 and 150 mm and inner diameter of 1.2 mm, constructed using borosilicate glass
55 tube, were molded as described in previous work.⁴⁴ The supports of the flow cells
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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 plat with dimensions of 5 x 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.

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A microcontroller PIC18F4550 model manufactured by Microgenios Microcontrollers (São Paulo, Brazil), which possesses digital interfaces 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.

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Others equipments and devices comprised a microcomputer furnished with RS 232 and USB serial interfaces, running a software 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;⁴⁵ 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.

42 43 44 *2.3. Experimental procedure*

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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 multicommutated approach was designed to fulfill this requirement. The diagram of the integrated system comprising the flow system and the photometer are depicted in Fig. 1.

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The control of the flow system and the data acquisition were assisted by a microcomputer running a software 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

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3 commands to handle the flow system module and to perform data acquisition. The
4 signal generated by the photometer was converted to a digital pattern by the
5 microcontroller and sent to the microcomputer through the serial interface. These
6 data were stored as an ASCII file to allow further treatment. While the analytical run
7 proceeded, a plot of the signal was displayed on the microcomputer screen to allow
8 its visualization at real time.
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13 Initially, the flow system module was in the standby condition, thus no
14 solution was flowing through it. When the software began the analytical run, each
15 mini-pump was switched on/off sequentially 20 times. This action was done to fill
16 each flow line that connect the mini-pumps to the reactors Rc_1 and Rc_2 with its
17 respective solution. Afterwards, the microcomputer inquired whether photometer
18 calibration would be performed. If calibration was required, the microcomputer
19 instructed the microcontroller to switch the mini-pump P_2 on/off 30 times in order to
20 fill the flow cell with the carrier solution (Cs). Afterwards, the signal (F_s) generated
21 by the photometer was read by the microcontroller and sent to the microcomputer. If
22 the F_s value was different from the value established as a reference ($S_r = 4000$
23 mV), the microcomputer requested the operator to adjust the signal magnitude F_s
24 to be equal to S_r . This was accomplished by turning the variable resistor coupled to
25 base of the transistor (Tr , Fig.1). The residual signal (R_s) related with diffuse
26 radiation⁴⁴ was achieved by filling the flow cell with compound solutions, which were
27 obtained by mixing 5 mL of solutions containing 50 and 75 mgL^{-1} V(IV) with equal
28 volumes of a 0.05% m/v ECR solution, producing a very intensely colored solution,
29 which were used to find the residual measurement.⁴⁴ If signals achieved while
30 maintaining flow cell filled with each solution were equal, we should consider that
31 the radiation into the flow cell was completely absorbed by the solutions, thus the
32 residual measurement (R_s) may be attributed to the diffused radiation.⁴⁴ The
33 measurements F_s and R_s were saved as references to be used for absorbance
34 calculation.
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50 After the calibration step, the analytical run proceeded following the mini-
51 pump switching pattern depicted in Fig. 1. In the first step (St_1), the mini-pump P_1
52 was switched on/off 5 times followed by an on/off switching action applied
53 sequentially to the mini-pumps P_2 and P_3 . This sequence of events as repeated in
54 step St_2 , was named here as a sampling cycle. The number of sampling cycles can
55 be increased to fill the reactor Rc_2 and flow cell with a mixture comprising sample
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3 and reagent solutions. The reactions to convert V(V) to V(IV) by ascorbic acid and
4 to form the compound to be detected, proceeded while the sample zone was
5 displaced through the reactor R_{C1} and R_{C2} toward the photometer (Det). The signal
6 generated by the photometer (Si), while steps St_1 , St_2 and St_3 proceeded was read
7 by the microcontroller by means of its analog-to-digital converter and sent to the
8 microcomputer. After absorption calculation, the data were saved as an ASCII file to
9 allow further treatment. While performing the sampling steps (Fig.1), only the carrier
10 solution (Cs) flowed through the flow cell, so that the signal generated is similar to
11 the reference signal (Sr), thus its record tended to be straight line that precede
12 signal related with vanadium concentration, which was generated while reading step
13 (St_3) proceeded.

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

3. Results and discussion

3.1. Absorbance calculation

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

$$27 \text{ Abs} = \log[(S_r - R_s)/(S_i - R_s)] = kcx$$

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29 Where:

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31 S_r = reference signal; R_s = residual measurement; S_i = signal related to the
32 current measurement; k = constant; c = analyte concentration; x = length of the flow
33 cell.

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3 While performing the calibration step, the Sr value was adjusted to be 4000
4 mV and the residual measurements (Rs) achieved using flow cells with optical
5 pathlengths of 50, 100, and 150 mm were 64.4, 85.6, and 95.3 mV, respectively. As
6 indicated in the experimental section, this assay was performed using two solutions
7 with different concentrations. The signals (Rs) generated with each flow cell
8 presented practically equal values, thus indicating that the radiation into the flow cell
9 was completely absorbed. In this sense, the generated signals could be considered
10 as residual measurements. In earlier work, it was demonstrated that when using an
11 LED based photometer, the range of accordance with the Bouguer-Lambert-Beer
12 law³³ should be widened by using the residual measurement for absorbance
13 calculation,⁴⁴ therefore this resource was employed in the current work.
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23 *3.2. Effect of the sample volume*

24 In a flow analysis system, the volume of the sample and reagent solution
25 exert an important role, because the volume of sample zone affects the dispersion
26 effect, while the ratio between volumes of sample and reagent solution can affect
27 the stoichiometry of the reaction. In this sense, an appropriate selection of both
28 sample zone volume and volume ratio of sample and reagent solution aliquots is
29 mandatory whether high sensitivity is a focus of the analytical procedures or not.
30 The volume of sample and reagent solutions aliquots was the first variable studied,
31 thus to achieve high sensitivity assays were carried out in order to find the better
32 ratio between volumes of sample and reagents solution aliquots. The results
33 indicated that the sample aliquot could be five times the volume of the reagent
34 solution without significant impairing of solutions mixing. Therefore, a sampling
35 cycle was established to include 5 strokes of the mini-pump P₁ followed by 1 stroke
36 of mini-pumps P₂ and P₃. Under this condition, the sample zone formed in the
37 reactor presented a sample volume 5 times higher than the volume of ascorbic acid
38 and erichrome cyanine R solutions. The number of sampling cycles was varied from
39 3 to 18, thus the volume of the sample zone varied from 210 to 1260 μL . This assay
40 was done using a 0.35 mgL^{-1} vanadium (V) solution, yielding the results shown in
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55 Analyzing these curves, we observed that from 15 sampling cycles, the
56 increases in signals were not significant, thus indicating that the volume of the
57 sample zone (1050 μL) was enough to lead the signal generated to a steady state
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condition. These results show that while volumes of sample zones increased five times, the gain in signals were about of 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.³³

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

3.2. Effect of the reagents 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 concentration ranging from 0.04 up to 2.00 mgL⁻¹, yielding the results shown in Table 1. Including results achieved using standard solutions with concentrations higher than 1.50 mgL⁻¹, a decrease in linearity was observed, thus their results were not considered.

Table 1. Effect of the reagent concentration

Concentration (%, w/v)	Concentration range (mgL ⁻¹)	Intersect	Slope (Lmg ⁻¹)	Linear coef. (r)
0.0017	0.04 – 1.50	0.0964	0.1040	0.9975
0.0035	0.04 – 1.50	0.1294	0.2321	0.9997
0.007	0.04 – 1.50	0.2248	0.3040	0.9997

0.014	0.04 – 1.50	0.4217	0.3087	0.9990
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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 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 increasing 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 43 %, the slope increased 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 the intersect increasing would not impaired the linear response range, the ECR concentration of 0.007% was selected.

Because eriochrome cyanine R reacted with vanadium (IV),⁴³ an ascorbic acid solution was mixed with sample aliquots in order to cause reduction of vanadium (V) to vanadium (IV). Intending to find adequate solution concentration, assays were done using ascorbic acid solutions with concentration of 0.25, 0.50 and 1.0 % (w/v) and a vanadium (V) standard solution with concentration of 1.50 mg L⁻¹. Results shown that there was no significant difference between the generated signals, whereby a 0.5 % (w/v) ascorbic acid solution was selected.

3.3. Effect of the pH

The carrier fluid (Cs) also functioned as a buffering solution, which was accomplished by switching on/off mini-pump P₂ 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 reacting 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 reacting 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 pH of 5.3 was selected.

3.4. Figures of merit related with 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.

Table 2. Figures of merit considering the optical pathlength of the flow cell

Evaluated parameters	Optical pathlength and inner volume		
	50 mm 58 μL	100 mm 113 μL	150 mm 170 μL
Linear range (mg L^{-1})	0.04 – 1.50	0.04 – 1.50	0.02 – 1.50
Linear correlation (r)	0.998	0.999	0.998
Limit of detection ($\mu\text{g L}^{-1}$)	20	16	13
Variation coefficient (%) ^a	0.69	1.58	0.87
Sampling throughput (h^{-1})	50	50	50
Chromogenic reagent (μg) [*]	11.6	11.6	11.6
Ascorbic acid (mg) [*]	8.6	8.6	8.6
Sample volume (μL) [*]	600	600	600
Waste generation (mL) [*]	2.4	2.4	2.4

^{*}Consumption and waste generation per determination; ^aResults achieved by performing 10 consecutive measurements using a mineral water sample spiked with $0.38 \text{ mgL}^{-1} \text{ V(V)}$.

Once the best working conditions were selected, including reagent solution concentration, acidity of reacting medium, and volumes of sample and reagent aliquots, a set of standard solutions was processed employing the flow cell with 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. 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, $13 \mu\text{gL}^{-1}$, was estimated using the 3σ criterion.⁴⁶ 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 and as well as uniformity of the records profile are very good, thus indicating a very good long-term stability.

3.5. Performance comparison

Comparing the performance of the proposed procedure with those presented by some existing spectrophotometric procedures for determination of vanadium, which are summarized in Table 3, we can observe that the current work affords significant advantages concerning to low volume of waste generation and high sampling throughput. Albeit limit of detection is higher than those presented in the referred works,^{10,12} it is 7 times lower than the maximum value recommended by the Brazilian regulatory agency for fresh water,⁴⁷ being also lower than the notification level ($15 \mu\text{L}^{-1}$) recommended by the Office Environmental Health Hazard Assessment (OEHHA) for drinking water.⁴⁸

Table 3. Performance comparison

Procedure	Linear range (mgL^{-1})	Limit of detection (μgL^{-1})	Sampling throughput (h^{-1})	Waste generation (mL)	Ref.
Flow analysis	0.02 - 1.50	13.0	47	2.4	*
Flow analysis	50 - 1500	-	30	6.8	3
Flow analysis	0 - 3.0	4.7	-	-	10
Flow analysis	0.05 – 1.2	15	10	28	16
Batchwise	0.01 - 0.45	3.2	-	100	12
Batchwise	0.1 – 2.8	12	-	10	2
Batchwise	0.50 - 5.30	16.8	-	10	18

*Current work

3.6. Study of the potential interferences

Intending to verify whether ions usually present in fresh water, such as Al^{3+} , Ni^{2+} , Pb^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Fe^{3+} , NO_3^- , SO_4^{2-} , Cl^- and F^- , 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 mgL^{-1} vanadium (V) standard solutions prepared with and without the potential interfering ions as related in Table 4.

Table 4. Effect of the potential interfering species

Chemical specie	Concentration (mgL^{-1})	Absorbance variation (%)
SO_4^{2-}	2.0	<5
Ni^{2+}	2.0	<5
Pb^{2+}	2.0	<5
Al^{3+}	20	<5*
Co^{+2}	2.0	<5
Mn^{2+}	300	<5
NO_3^-	150	<5
Zn^{2+}	2.0	<5
Cl^-	500	<5
F^-	2.0	<5
Fe^{3+}	50	<5*

Maximum assayed value; *100 $\text{mg L}^{-1} \text{ F}^-$

Taking an absorbance variation of $\pm 5\%$ as a criterion for interference and employing the absorbance generated processing a 1.0 mgL^{-1} vanadium (V) standard solution as a reference, we can observe that only Al^{3+} and Fe^{3+} 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. 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 for samples showed that concentrations would be lower than the limit of detection ($13 \mu\text{gL}^{-1}$). The samples were also analyzed employing graphite furnace atomic absorption spectrometry (GF AAS), the results were also lower than the limit of detection ($3 \mu\text{gL}^{-1}$). For this reason, the recovery method was applied in order to allow accuracy assessment, yielding the results shown in Table 5.

Table 5. Analytical results of the recovery tests

Sample	Added amount (mgL^{-1})	Found amount (mgL^{-1})	Recovery (%)
River water			
1	0.50	0.462 ± 0.022	92.36
2	0.50	0.475 ± 0.023	94.94
3	0.50	0.470 ± 0.014	93.96
4	0.50	0.440 ± 0.024	87.18
5	0.50	0.493 ± 0.017	98.62
Mineral water			
6	0.38	0.338 ± 0.001	88.86
7	0.38	0.349 ± 0.023	91.79
8	0.38	0.397 ± 0.004	104.52
9	0.38	0.382 ± 0.027	100.52
10	0.38	0.416 ± 0.002	109.45

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.^{40,41,42}

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3 The use of an LED based photometer furnished with a flow cell of long optical
4 pathlength shows to be an effective strategy to increase sensitivity, allowing
5 improvement at the limit of detection without using of laborious pre-concentration
6 steps, resource that has been usually employed.^{7,10,12,17} The proposed setup
7 afforded cost-effective, operational simplicity and as well as a low reagent
8 consumption (11.6 µg of ECR per determination), therefore indicating that it would
9 become a suitable alternative for monitoring of vanadium in sample of
10 environmental interest.
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Caption of figures

Figure 1. Diagram of the photometer and flow system assembling. LED = Light Emitting Diode, $\lambda_{\max} = 560 \text{ nm}$; I_a and I_b = radiation beams emitted by the LED and coming out from the flow cell; Tr = transistor BC547; Dz = Zener diode, 3.2 V; fb = flow cell body of borosilicate glass tube, 1.2 mm inner diameter; fp = fusing point; h = flow cell length, 150 mm; Det = photodetector OPT301; IA = instrumentation amplifier; Si = output signal in mV; D_1 and D_2 = rectifier diodes 4007; R_s = gain resistor. S = sample solution, Cs = carrier fluid, 0.5 % ascorbic acid solution; R = chromogenic solution; P_1 , P_2 and P_3 = solenoid mini-pumps; V = three-way solenoid valve; Rc_1 and Rc_2 = reaction coil, length of 20 and 40 cm, respectively; W = waste. Flow lines and reaction coils were of polyethylene tubing, 0.8 mm inner diameter. T_1 , T_2 and T_3 = timing course to switch on/off solenoid mini-pumps P_1 , P_2 , and P_3 , respectively. Shadow surfaces beneath of the timing lines indicate that the respective device is switched on.

Figure 2. Effect of the sample volume for different flow cells length. Numbers refer to the optical pathlength of the flow cells.

Figure 3. Effect of the pH on the signal. Results obtained by processing a vanadium (V) standard solution with concentration of 0.35 mgL^{-1} .

Figure 4. Record of the measurements. From left records are related with standard vanadium (V) solutions with concentration of 0.00, 0.02, 0.04, 0.09, 0.19, 0.38, 0.75 and 1.00 mg L^{-1} .

Figure 1.

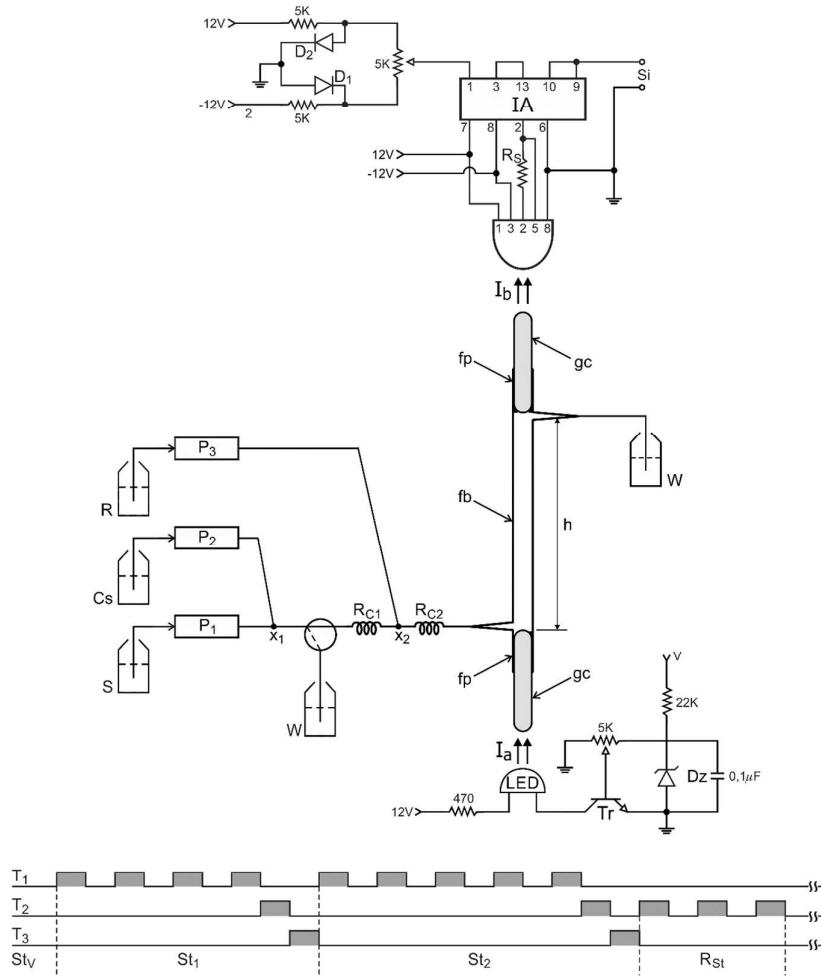


Figure 2.

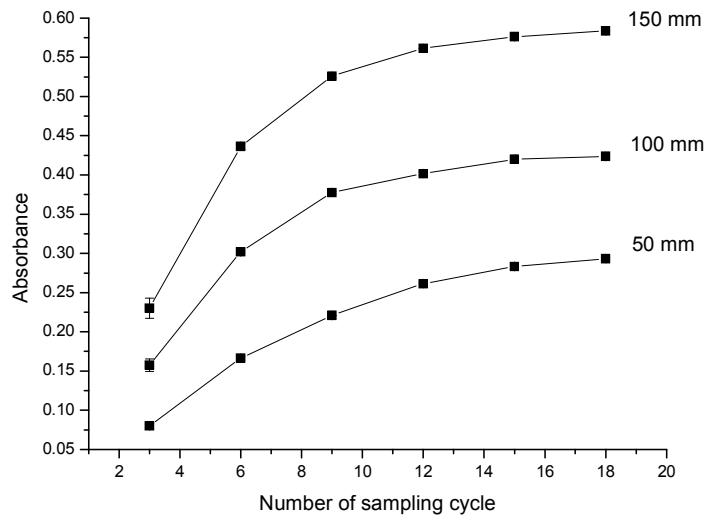
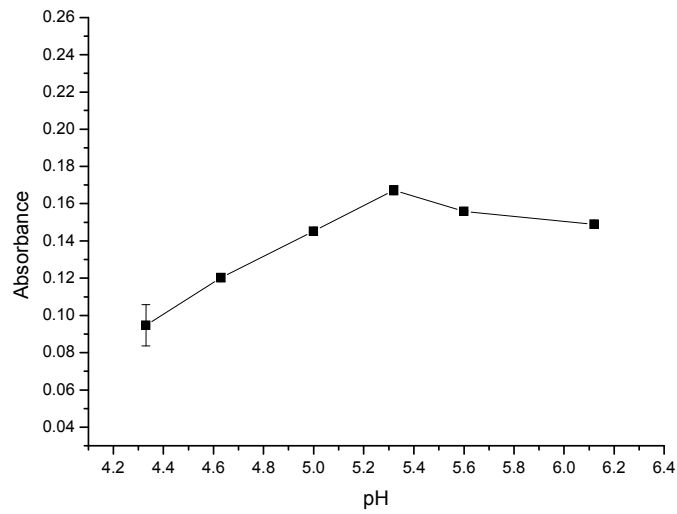


Figure 3.



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Figure 4.

