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Use of dimethylglyoxime for the spectrophotometric flow-based determination of nickel in natural waters

Tânia C.F. Ribas, Raquel B.R. Mesquita, António O.S.S. Rangel *

CBQF - Centro de Biotecnologia e Quwímica Fina - Laboratório Associado, Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Diogo Botelho, 1327, Porto 4169-005, Portugal

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ABSTRACT

A spectrophotometric flow-based method for the determination of nickel in recreational waters is proposed. In this scenario, the strategy was to devise a miniaturized and automatic system based on sequential injection analysis, aiming for an expeditious, real-time and low-cost determination. For the spectrophotometric determination, dimethylglyoxime was used as color reagent due to its selectivity for nickel. Considering the expected low concentration and low sensitivity of the coloured reaction, a long pathlength flow cell was used to increase the sensitivity. The potential interference of metal ions commonly present in freshwaters was assessed and no significant differences (<10%) were observed, except for manganese. This interference was overcome by adding manganese to the reagent, thus acting as a fixed interference strategy. The limit of detection and quantification were 6.3 and 21.1 μg L^{-1}, respectively. The method was applied to the quantification of nickel in certified water samples and the results were in agreement with the certified values. Additionally, the method was successfully applied to the quantification of nickel in spiked freshwaters and the results were in agreement with those obtained with the reference method.

Introduction

Nickel determination in water is mostly based on the use of flame atomic absorption spectrometry (FAAS), electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma - optical emission spectrometry (ICP-OES) and inductively coupled plasma – mass spectrometry (ICP-MS), with detection limits of 6, 0.07, 0.4 and 0.00006 μg L^{-1} respectively [1–3]. Despite the low and ultra-low limits of detection associated, these methods involve sophisticated and expensive equipment, high maintenance costs, and require skilled operators. Therefore, the molecular absorption spectrophotometric based methods seem to be appealing in analytical chemistry due to the associated features of this technique, when compared with the aforementioned analytical methods. The main advantages are the simplicity, versatility, robustness, accuracy and low cost [4], making the molecular absorption spectrophotometry one of the most commonly detection methods used in the lab routine. Despite these features, the limit of detection that can be achieved may not meet the levels for the targeted type of sample. This is the case for nickel, for which no spectrophotometric methods are pointed out in reference procedures for water monitoring [1] and, as far as we now, there are only a few flow-based systems with spectrophotometric detection [5,6]. In addition, these flow-based works were devoted for the analysis of plants and biological samples.

Nickel is usually present at trace levels in surface waters (maximum expected concentration of 100 μg L^{-1}), which makes it an extra challenge in analytical chemistry. To overcome these difficulties, different strategies can be followed to improve the sensitivity and/or to improve the limit of detection. One of the strategies, very often used in analytical chemistry, is solid phase extraction (SPE). This is considered a very versatile technique for sample preparation and the main objective is the sample matrix removal and/or enrichment of the target analyte, enabling the increase of sensitivity and selectivity [7–10]. However, some drawbacks are associated with the use of this technique in a flow-based approach, such as the decrease on sample analysis throughput, the preferential pathways and the increased backpressure [10]. Another potential strategy, that aims the increase of the sensitivity of a spectrophotometric method in flow analysis, is the use of cells with increased pathlength such as the liquid waveguide capillary cell (LWCC) [11]. Thereby, with the use of a LWCC, the optical pathlength can be increased up to 500 times when compared with a typical 1 cm pathlength flow cell, increasing the absorbance signal and consequently the

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* Corresponding author.
E-mail address: arangel@ucp.pt (A.O.S.S. Rangel).

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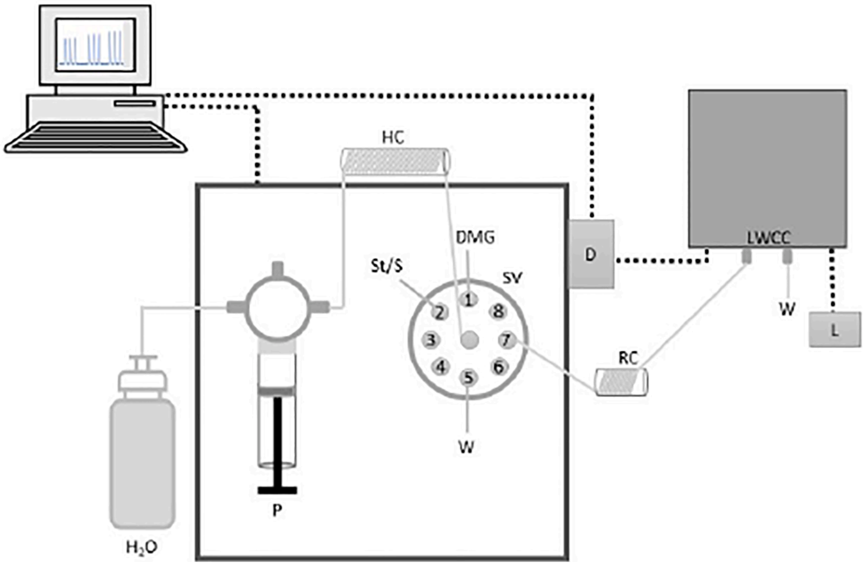

Fig. 1. Flow manifold for Ni(II) determination in freshwaters. St/S – standard or sample solution; DMG – 1.0% dimethylglyoxime solution in 0.75 mol L^{-1} NaOH solution; P – syringe pump; SV – selection valve; HC – holding coil; RC – reaction coil (50 cm); D – Ocean Optics Flame UV/Vis CCD detector; L – light source; LWCC – liquid waveguide capillary cell (100 cm path length); W – waste.

sensitivity, and lowering the limit of detection [11].

Nickel occurs ubiquitously and naturally in the environment, it can be found in the soil, water, and air. Nickel is an attractive metal with several applications in the industry, due to its associated characteristics, as it forms useful alloys with a variety of other metals [12,13]. Because of nickel's great use, it can be easily released into the environment, reaching water sources and the soil. Additionally, its mobility is increased in the soil under acidic conditions, and consequently can easily reach groundwater [12]. Nickel is considered an essential element for animals, being its deficiency associated with an altered liver functioning. However, exposure to high levels of this metal (metallic nickel or nickel soluble or less soluble compounds) is associated with human harmful effects, such as allergic reactions, asthma, lung cancer and leukaemia [12,14].

In the present work, a spectrophotometric method for the determination of nickel in recreational freshwaters is proposed. As colorimetric reagent, an option was made to select dimethylglyoxime (DMG), a reagent that forms a pink complex with nickel. DMG displays high selectivity for nickel, mostly applied for its gravimetric quantification [15,16]. The strategy was to devise a miniaturized and automatic system based on sequential injection analysis, targeting an expeditious, real-time and low-cost determination. As far as we know, no flow-based system was reported for the use of DMG as colorimetric agent. Flow-based methods seem to be particularly interesting to employ this type of strategy due to the intrinsic characteristics of the systems, such as versatility, use of low volumes of reagents and sample, the increased analysis throughput, and also the possibility of signal acquisition be performed without chemical equilibrium [17,18]. Additionally, considering the expected low concentration of nickel in recreational waters, the use of a LWCC with a 100 cm optical pathlength was used to improve the sensitivity of the method.

Table 1
Protocol sequence for the Ni(II) determination in recreational waters.

Step	SV position	Volume (μL)	Flow-rate (μL/s)	Description
A	2	300	10	Aspirate standard/sample solution
B	1	75	10	Aspirate DMG working solution
C	7	1300	10	Propel through the LWCC for Ni (II) detection

Material and methods

Reagents and solutions

All solutions were prepared with analytical grade chemicals and MilliQ water, MQW (resistivity > 18 MΩ cm, Millipore, USA).

A stock solution of 50.0 mg L^{-1} of Ni(II) was prepared by dilution of the respective 1000 mg L^{-1} atomic absorption standard solution (Fluka, Germany). An intermediate stock solution of 500.0 μg L^{-1} of Ni(II) solution was prepared by dilution of the stock solution. Working standards from 25.0 to 150.0 μg L^{-1} with 0.01 mol L^{-1} of nitric acid were weekly prepared by proper dilution of the intermediate stock solution.

A 1.0% of dimethylglyoxime (DMG) solution was prepared by dissolution of the corresponding quantity of the reagent (Sigma-Aldrich, Germany) in 0.75 mol L^{-1} mL sodium hydroxide. A 50 mg L^{-1} Mn(II) standard was prepared by diluting the 1000 mg L^{-1} commercial atomic absorption standard solution with water (Merck, Germany). A 5.0 mL DMG working solution with 0.25 mg L^{-1} of Mn(II) was daily prepared by adding 25 μL of a 50 mg L^{-1} of Mn(II) standard (please see section 3.3).

A 0.01 mol L^{-1} nitric acid solution was prepared by dilution of the concentrated solution (rd = 1.39; 65%, Merck, Germany).

A 0.75 mol L^{-1} sodium hydroxide solution was prepared by dissolution of the corresponding quantity of the solid (Panreac, Spain) in water.

All solutions used for the interferences assessment (Al(III), Ca(II), Co(II), Cr(III), Cu(II), Fe(III), Mg(II), Mn(II) and Zn(II)) were prepared by diluting the commercial atomic absorption standard solution (1000 mg L^{-1}, Merck, Germany).

Apparatus

A MicroSIA equipment controlled by a computer SIAsoft software (FIAlab Instruments, USA) was used. This sequential injection system was equipped with a 2.5 mL syringe pump connected to the central channel of an eight-port selection valve (Valco VICI Cheminert® 170–0317 L, USA), an Ocean Optics Flame UV/Vis charged coupled device (CCD) spectrophotometer detector and an Ocean Optics halogen light source (HL-2000, USA). The selection valve of the flow-based system was coupled to a liquid waveguide capillary cell (LWCC, 100

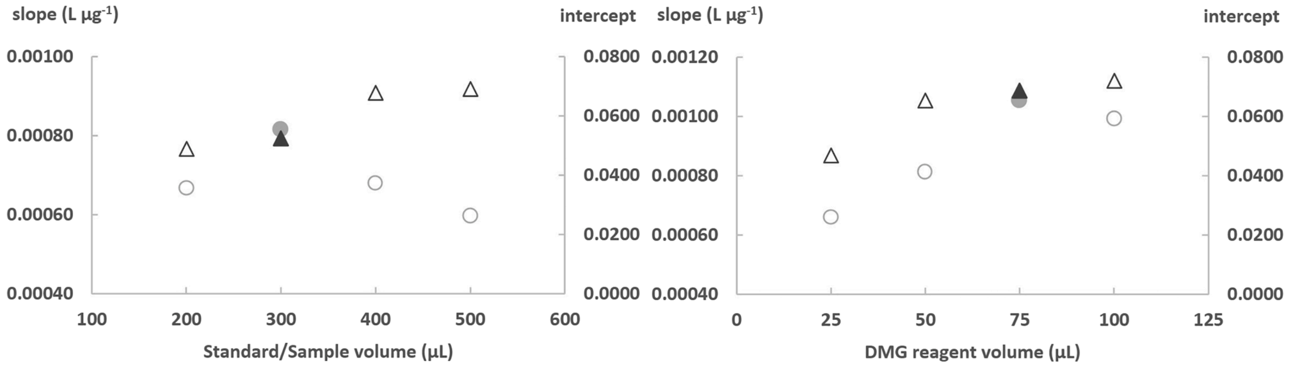

Fig. 2. Study of the influence of the standard/sample (St/S) volumes and dimethylglyoxime (DMG) reagent on the sensitivity (calibration curve slope - circles), and on the calibration curve intercept (triangles). The chosen volumes are presented by blacked-filled markers.

cm path length, 300 µL inner volume – World Precision Instruments, USA). The LWCC was coupled to the light source and the CCD detector, using fiber optic cables, for absorbance measurement. All the components of the flow system were connected by PTFE tubing from Omnifit (0.8 mm i.d., UK).

Flow manifold and procedure

The developed flow-based manifold for the quantification of Ni(II) in freshwaters is depicted on Fig. 1 and the method protocol is shown in Table 1. The standard/sample and the reagent solutions were aspirated through the selection valve to the holding coil (3.0 m of coiled tubing - 1.5 mL capacity) and subsequently sent to the LWCC for detection trough the reaction coil (0.5 m of a knotted reactor with 0.25 mL capacity).

Water samples collection and preparation

Sampling campaigns were performed in various recreational locations from Douro River, Porto district (Portugal). Superficial water samples were collected in 500 mL acid-cleaned polyethylene bottles.

Key physical and chemical parameters, namely temperature, conductivity, salinity, pH, oxygen saturation and turbidity were measured *in situ* using a YSI6920 CTD multiparameter probe.

The samples were filtered with Acrodisc 25 mm syringe filters 0.45 µm (Pall, USA) and acidified to the pH of 2 with nitric acid solution, as recommended by the reference procedure for sampling and storage of waters for metals quantification [1]. Samples were kept refrigerated until analysis.

Method validation

For comparison purposes, the determination of Ni(II) in freshwaters was also carried out by a reference procedure, resorting to inductively coupled plasma – optical emission spectrometry (ICP-OES) [1], in a Perkin Elmer Optima 7000 dv (USA) equipment. Results were compared with those obtained with the developed flow-based method.

Additionally, the developed flow method was applied to the analysis of certified wastewater samples available for the determination of trace elements: SPS-WW1 Batch 120 and SPS-WW2 Batch 116 (Labmix24 GmbH, Germany). The certified water samples were diluted in order to fit the linear range of the calibration of the developed method.

Results and discussion

Preliminary studies

Regarding the spectrophotometric determination of Ni(II), some preliminary studies were made involving the DMG reagent prepared with different matrices suggested in the literature, namely sodium hydroxide and alcohol [15]. These two DMG solutions were tested for nickel quantification and the performance evaluated in terms of sensitivity (calibration curve slope). By using DMG prepared in alcohol (96%), the sensitivity was lower and the absorbance signal was null for the Ni(II) standard concentration equal or lower than 2.5 mg L^{-1}. When the DMG solution was prepared in a 3% NaOH solution, a calibration curve for Ni(II) within the range of 0.10–1.0 mg L^{-1} was performed. The absorbance signal reached the maximum value only after 30 min with no significant differences up to 1 h. The maximum absorbance signal was achieved at the wavelengths of 390 and 460 nm. The calibration curve slope was higher at 390 nm, and so this was the chosen wavelength for further studies. The DMG prepared in hydroxide was chosen to continue the development of the flow-based strategy. Additionally, with the purpose of improving the sensitivity of the determination, a long pathlength flow cell (LWCC with 100 cm optical path) was used.

Development of the flow-based system

The development of the flow-based system involved several studies to evaluate the effect of some physical and chemical variables on the method performance using a univariate approach. The flow parameters were established regarding the improvement of the calibration curve parameters, by combining the highest calibration curve slope (sensitivity) with the lowest intercept. Additionally, the flow parameters were also chosen regarding the possibility of increasing the determination rate and minimize the quantities of sample and reagents used, without compromising the analytical features. The evaluated parameters were: the volumes of standard and DMG solution; the DMG solution concentration; the flow-rate when propelling through the LWCC, and the reaction coil length.

The development of the flow-based system began with the study of the effect of using different volumes of standard (concentration range from 25 to 150 µg L^{-1}) and the 1% DMG solution at the calibration curve parameters. The studied volumes varied from 200 to 700 µL for the standard solution and 25 to 100 µL for the DMG solution. The volumes of standard and DMG solutions selected to continue the method development were 300 and 75 µL, respectively. These results are summarized in Fig. 2.

Different concentrations of the DMG solution were also tested: 0.25, 0.50, 1.0 and 2.0%. Better features were observed by using the 1.0% concentration; a higher slope was obtained in comparison with the calibration curves using the other tested concentrations (difference > than 10%) and better repeatability between standard replicas (relative standard deviation between replicas lower than 5%).

The reaction coil length was also studied (25, 50 and 75 cm), and the 50 cm reaction coil was the one selected. With the use of the 25 and the 50 cm reactor, the slope of the calibration curve did not differ significantly (difference <5%), however the intercept is lower for the 50 cm

Table 2

Study of the interference (in percentage of the signal) of some metal ions, commonly present in natural waters, in the nickel determination. Comparison of the absorbance signal between a 50 μg L^{-1} Ni^{2+} standard concentration with the signal from a 50 μg L^{-1} Ni^{2+} standard concentration containing the potential interfering species.

Tested ion	Water streams*(mg L^{-1})	Ratio tested (Me:Ni)	Interference percentage (%)
Al^{3+}	0.4	4	−7.4
Ca^{2+}	15	200	−2.5
Co^{2+}	0.01	0.2	+4.4
Cu^{2+}	0.1	2	−8.5
Fe^{3+}	0.7	2	+8.6
Mg^{2+}	4	80	−6.0
Mn^{2+}	0.1	0.5	+59
		2	+70
Zn^{2+}	0.1	1	−2.6

*Maximum expected concentration in streams [1].

Table 4

Comparison of the results obtained with the developed flow system for nickel determination ($[Ni^{2+}]_{FA}$) in certified water samples with the certified values ($[Ni^{2+}]_{certified}$).

Sample ID	$[Ni^{2+}]_{certified}$ mg L^{-1}	$[Ni^{2+}]_{FA}$ mg L^{-1}	RD%
SPS-WW1	1.000 ± 0.005	1.02 ± 0.07	+2.2
SPS-WW2	5.000 ± 0.025	4.71 ± 0.15	−5.8

Table 3

Features of the developed flow-based system for nickel quantification in recreational waters. A, absorbance; SD - standard deviation; LOD, limit of detection; LOQ, limit of quantification.

Dynamic range (μg L^{-1})	Calibration curve[a] A = (slope ± SD) μg L^{-1} Ni^{2+} + intercept ± SD	LOD (μg L^{-1})	LOQ (μg L^{-1})
25.0 – 150	$A = (1.06 \times 10^{-3} \pm 4 \times 10^{-5})\ Ni^{2+} + 0.0786 \pm 0.072$	6.3	21.1

[a] $n = 5$.

reaction coil (difference > 10%). By using the 75 cm reaction coil, both calibration features are lower (difference > 15%) than with the 50 cm. So, the reaction coil of 50 cm length was selected.

The flow-rate used to propel the plugs of reagent and standard through the flow cell was also assessed (10, 15 and 20 μL s^{-1}). By propelling the solutions plugs at a 10 μL s^{-1}, a lower relative standard deviation between replicas (<5%) was obtained.

Interference studies

A study to evaluate the potential interference of some metal ions in the determination of Ni(II) was performed and assessed as interference percentage (IP). This was attained by comparing the absorbance signal of a 50 μg L^{-1} Ni(II) standard with the absorbance signal from a 50 μg L^{-1} Ni(II) standard with the potential interfering species added. The potential concentration of interfering species in water streams and the tested ratio to the 50 μg L^{-1} Ni(II) standard are depicted in Table 2.

No significant interferences (IP < 10%) were observed for all the metal ions in this interference study with the exception for manganese. The manganese can be present in surface waters in a concentration up to 100 μg L^{-1} [1] and it interferes positively with Ni(II) quantification (IP > 50%) even when present at low concentrations (Mn ≈ 25 μg L^{-1}). To assess the extension of this problem, a calibration curve in Mn(II) standards within the same concentration range of Ni(II) standards (25 – 150 μg L^{-1}) was performed. The absorbance signal for all the Mn(II) standard solutions did not differ significantly from the absorbance signal from the blank solution and so, this indicates that manganese did not form a coloured product with the DMG reagent. So, at this point, some other studies were performed to evaluate how the presence of manganese interfered with the reaction of nickel with the DMG reagent, and subsequently some strategies were also explored to minimize this interference. Firstly, some spectra were performed resorting to a conventional spectrophotometer. The spectra corresponded to solutions containing: (i) 3 mg L^{-1} Ni(II) solution and the DMG solution; (ii) 3 mg L^{-1} Mn(II) solution and the DMG solution; and (iii) 1.5 mg L^{-1} Ni(II) plus 1.5 mg L^{-1} Mn(II) solution and the DMG solution. The solution that only contained manganese(II) and DMG showed a maximum absorbance signal at 390 nm. When the solution contained nickel(II), two different wavelengths with maximum absorbance signal, 390 and 460 nm were observed. The chosen wavelength to perform nickel determination until this point was 390 nm, as it corresponded to the highest sensitivity. However, due to the aforementioned study, at the wavelength of 460 nm the interference of Mn(II) was minimized. So, the wavelength to perform nickel detection in the flow-based method was switched to 460 nm. The study of volumes of standard and DMG reagent was carried out again, and the already volumes set for the flow-based strategy were confirmed. The possible interference of manganese was assessed once again and, even though the interference was minimized in these conditions, the presence of manganese still interferes positively (IP > 10%) in the nickel determination. Another study was then performed to further minimize this interference; the idea was to buffer the presence of manganese by adding a pre-set quantity to the reaction media; this way, the extent of interference was fixed. To achieve this purpose, the DMG reagent was prepared with different concentration of manganese, 0.050, 0.25 and 1.0 mg L^{-1}. Different standards were prepared, and calibration curves were performed with the different DMG solutions. The standards used to evaluate if the manganese still interfered in the nickel determination were: (a) Nickel standards solutions (0 - 100 μg L^{-1}); (b) Nickel standards solutions (0 - 100 μg L^{-1}) with 50 μg L^{-1} of manganese; (c) Manganese standards solutions (0 - 100 μg L^{-1}) with 50 μg L^{-1} of nickel. When the standards of manganese were introduced (c), the absorbance signal for all the standards was not significantly different from each other and from the blank solution absorbance. By using the DMG reagent prepared with 0.25 mg L^{-1}, no significant differences (< 10%) were observed between the calibration curves performed with the standards with just nickel (a) and the standards of nickel with manganese (b). So, with this strategy, the interference of manganese was minimized (IP < 10%).

Analytical features

The analytical features of the developed sequential injection system for the determination of Ni(II) in freshwaters are summarized in Table 3.

For the limit of detection (LOD) and the limit of quantification (LOQ) assessment, the IUPAC recommendations were considered. These concentration values were calculated as the concentration corresponding to the sum of three and ten times (for LOD and LOQ respectively) the standard deviation to the mean value of ten consecutive blank solution measurements [19,20].

The repeatability of the absorbance measurement of a particular Ni (II) solution was assessed by the calculation of the relative standard deviation (RSD) of ten replicate analysis of a standard (50 μg L^{-1}) and a water sample. A RSD of 2.5% for the standard solution and 1.4% for the sample solution was attained.

A complete analytical cycle (three replicas) for the determination of

Table 5
Application of the method to the analysis of spiked freshwaters from various recreational locations from Douro River, Porto district (Portugal). Comparison of the results obtained with the developed flow-based system ($[Ni^{2+}]_{FA}$) and with the reference method ($[Ni^{2+}]_{Ref}$) for nickel determination; RD, Relative deviation.

Sample ID	$[Ni^{2+}]_{Ref}$ µg L^{-1}	$[Ni^{2+}]_{FA}$ µg L^{-1}	RD%
#1	44.1 ± 1.4	42.8 ± 0.3	−2.9
#2	96.0 ± 1.6	104.2 ± 1.7	+8.5
#3	61.0 ± 2.3	64.4 ± 5.1	+5.6
#4	81.1 ± 1.9	74.9 ± 0.6	−7.6
#5	43.5 ± 0.2	48.5 ± 0.4	+11.5
#6	74.0 ± 1.8	88.1 ± 0.0	+9.6
#7	52.3 ± 0.4	45.7 ± 0.3	−12.6
#8	85.5 ± 1.8	82.9 ± 1.4	−3.0

Ni(II) took about 5 min. The corresponding reagents consumption for an analytical cycle was: 2.3 mg of DMG, 6.8 mg of sodium hydroxide and 0.056 µg of manganese.

Determination of Ni(II) in waters

For accuracy assessment, the developed flow-based system was applied to determination of Ni(II) in certified water samples. The relative deviation between the certified value and the one obtained with the herein proposed system was below 10% for both certified water samples, validating the developed method for Ni(II) determination (Table 4).

Since the Ni(II) concentration of the analyzed freshwater samples were found to be below the limit of detection of the developed method and/or the reference procedure (ICP-OES), water samples were spiked with unknown quantities of nickel (II); then, the spiked samples were analyzed by the developed flow-based method and the reference method ICP-OES. The validation was attained by comparison between the two set of results. The Ni(II) concentrations obtained with the two different procedures and the comparison results (relative deviation – RD) are displayed in Table 5. A linear regression equation was established between the two set of results, the ones obtained with the developed flow-based system ($[Ni^{2+}]_{FA}$ µg L^{-1}) and the reference method ($[Ni^{2+}]_{Ref}$ µg L^{-1}). The established linear regression equation was $[Ni^{2+}]_{FA} = 1.05\ (\pm 0.12)\ [Ni^{2+}]_{Ref} + 2.52\ (\pm 8.24)$, where the values in brackets represents the 95% confidence interval. These parameters showed that the estimated slope an intercept did not differ statistically from 1 to 0 respectively and so, there were now significant differences between the results obtained with the developed flow-based system and the reference method [21].

Conclusion

The developed spectrophotometric flow-based method for nickel quantification in natural waters proved to be an efficient tool for water monitoring. The molecular absorption spectrometric methods bring advantages over the high sophisticated and expensive methods commonly used for this determination (FAAS, ETAAS, ICP-OES and ICP-MS). When compared with these methods, the main advantages associated with the developed spectrophotometric flow-based system are the simplicity, versatility, accuracy, low-cost and low reagents consumption. There are few works describing flow-based methods for the quantification of nickel, but these were devoted for the analysis of biological samples and plants [5,6]. In these methods, a non-selective reagent was employed, the 2-(5-bromo-2-pyridylazo)−5-diethylaminophenol (Br-PADAP). To overcome the low selectivity, the use of extra techniques/reagents to mask interferences is mentioned in the published works. Additionally, both works are based on flow injection analysis where is implicit the continuous reagents consumption. Oppositely, in the herein described method, the sequential injection approach minimizes the quantities of reagents/sample usage. By using the DMG reagent, a higher selectivity for nickel is displayed when compared with Br-PADAP, also minimizes the steps for the determination and the use of extra reagents to mask interferences. In the herein proposed method, the interference of manganese could be seen as a limitation, nevertheless it was minimized by adding a pre-set quantity of this ion to the DMG reagent. This strategy acted as a masking approach of manganese and did not bring any extra step as the masking agent is present in the reagent solution itself. Additionally, the low limits of detection and quantification achieved are far below the 1.4 mg L^{-1} screening value in recreational waters and the 0.07 mg L^{-1} for the drinking water guideline proposed by the World Health Organization (WHO 2021) [22]. The developed method was applied for the determination of nickel in certified water samples and to spiked natural waters, and the results were in agreement with the expected values.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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