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A modification of the dimethylglyoxime method for Nickel determination: Application in bioremediation processes

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ABSTRACT

Background: Environmental contamination with nickel is increasing due to the discharge of industrial effluents and other anthropogenic activities. Therefore, the improvement of methods for monitoring nickel concentration is of great value. The dimethylglyoxime (DMG) method is used to determine the nickel concentration in aqueous solutions. This method requires the oxidation of Ni(II) to Ni(IV) by bromine water before adding DMG, which is necessary to complete color development. The original method uses more than 50 mL of final reagent volume per sample. In this study, a volume reduction of the DMG method was performed.
Results: A volume reduction of 1 mL per sample was successfully achieved for the DMG method. The working range was 0 - 10 mg Ni(II) L^{-1}. The specified limits of detection and quantification (LOQ and LOD) were 1.18 and 0.41 mg L^{-1} respectively. A comparative analysis with atomic absorption spectroscopy (AAS) showed no significant differences between both methods for nickel determination. The modified DMG method was effective for the measurement of nickel in experimental samples from a bioremediation assay.
Conclusion: The modified DMG method offers considerable advantages. The modified method reduces the volume of reagents used from 50 mL to just 1 mL. The requirement of smaller volume of each reagent is economically favorable, and consequently the amount of passive waste generated is reduced. It is easily reproducible in a laboratory with access to a spectrophotometer and simple reagents. In addition, the possibility to measure samples from bioremediation assays is an advantage.

1. Introduction

Environmental contamination with nickel has become a worldwide problem due to its active role in industry [1]. Nickel has harmful effects on humans and other organisms, that have been extensively studied [2]. Natural ecosystems often have low nickel concentrations, due to weathering of rock and soil and atmospheric deposition. In surface waters nickel is found at trace levels, with a maximum expected concentration of 100 μg Ni(II) L^{-1} [3]. Though, significant amounts of this metal are introduced into the environment through poorly regulated disposal of wastewater [2]. Therefore, special attention must be given to ensuring compliance with effluent discharge regulations and maintaining acceptable environmental concentrations. In this sense, monitoring of nickel levels in aqueous solutions is an important issue.

The most commonly used analytical methods for the detection of trace metal ions are inductively coupled plasma-mass spectrometry (ICP-MS) and AAS [4]. These are powerful and sensitive methods. However, these methods are expensive and require experienced analysts and time-consuming sample preparation. For this reason, the improvement of effective, reliable, simple, and ideally inexpensive techniques for monitoring metal ion concentrations are very valuable. In particular, the analysis of metals in different types of samples is crucial to fulfill

Abbreviations: DMG, dimethylglyoxime; AS, algal strain; AAS, atomic absorption spectrometry; ICP-MS, inductively coupled plasma-mass spectrometry; LOD, limit of detection; LOQ, limit of quantitation; SD, standard deviation.

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present environmental requirements. Colorimetric methods are an interesting alternative at this point, especially for nickel detection [5].

The DMG colorimetric method has been successfully used for the detection and quantification of nickel in various studies [6–10]. The method is based on the formation of a soluble red-orange complex by the reaction between nickel ions and DMG. To achieve this, bromine water is added in the sample for complete oxidation of nickel, then an ammonium hydroxide solution is used to neutralize excess of bromine and adjust the pH before adding the DMG solution for color development. This complex has maximum absorbance at 445 and 543 nm [11]. Although the DMG method has been proven effective for detecting nickel in solution, the fact that uses a large quantities of reagents, over 50 mL per sample, could represent a drawback [12–14]. In addition, this method has only been used in a few studies for complex samples analysis [7,9,10]. Several authors have explored alternatives to overcome these limitations; for example, some studies have focused on developing nickel sensors [15], paper detection systems [16,17], solid-phase extraction [18], and flow-based determination for the analysis of nickel samples [3,19]. In this scenario, it is useful for the scientific community to have a simple technique that can be easily replicated.

In this sense, motivated by the need for a rapid, inexpensive and more accessible method, environmentally friendly and suitable for the analysis of complex samples, we performed a volume reduction of the method developed in the paper '*Colorimetric Determination of Nickel with Dimethylglyoxime*', by Mitchell et al. [11]. In addition, we evaluated the performance and accuracy of the modified method in the analysis of experimental samples. These samples correspond to the supernatant of a bioremediation process with unicellular algae treated with a formulated medium with a known nickel concentration. Unicellular algae are an extensive group of photosynthetic microorganisms that have been widely studied for bioremediation applications. The algae strains used in this work were isolated from metal contaminated environments. All the strains belonged to the division chlorophyte, colloquially known as green algae, commonly used for bioremediation processes [20–22].

2. Material and methods

2.1. Reagents

All chemicals were of analytical grade and commercially available from Sigma-Aldrich (USA) unless a different supplier is specified: ammonium hydroxide (NH_4OH) 5 % v/v, prepared from a 28–30 % commercial solution; absolute ethanol (C_2H_5OH) (Anedra, Argentina); bromine water ($Br_{2(aq)}$) 0.22% m/v: 1.1 g of potassium bromide (KBr) was dissolved in 10.7 mL of 1 M hydrochloric acid (HCl). Then 7.6 mL of sodium hypochlorite (NaClO) was added, and finally, the mixture was diluted with 32 mL of deionized water (0.13 μS cm^{-1}); DMG anhydrous 0.1% m/v: 0.1 g of the reagent was made up to 100 mL with absolute ethanol; nickel standard (0.1 g L^{-1}): $NiCl_2{\cdot}6H_2O$ was weighed in an analytical balance and diluted with deionized water. The standard was acidified to a final concentration of 0.5 % v/v HNO_3.

2.2. Modified DMG analytical procedure

First, 100 μL of the sample was mixed with 230 μl of bromine water, which turns the solution orange. This reagent is added to ensure the oxidation of Ni(II) to Ni(IV). Then 100 μl of NH_4OH was added, making the solution colorless again. Next, 170 μl of absolute ethanol was incorporated since the intensity and color stability of the reaction depends on its concentration. Finally, 400 μl of DMG was added to the Eppendorf tube. This compound forms the Ni-DMG complex, which gives the solutions its characteristic orange color. The samples were mixed after the addition of each reagent. Fig. 1 shows the summary of the entire procedure described above. After incubation (Section 3.3), the absorbance was measured in the spectrophotometer at 445 and 543 nm. All absorbance spectra were collected using a UV-1800 SHIMADZU spectrometer and *UV Probe 2.43* software. PMMA plastic cuvettes with a path length of 1.0 cm were used.

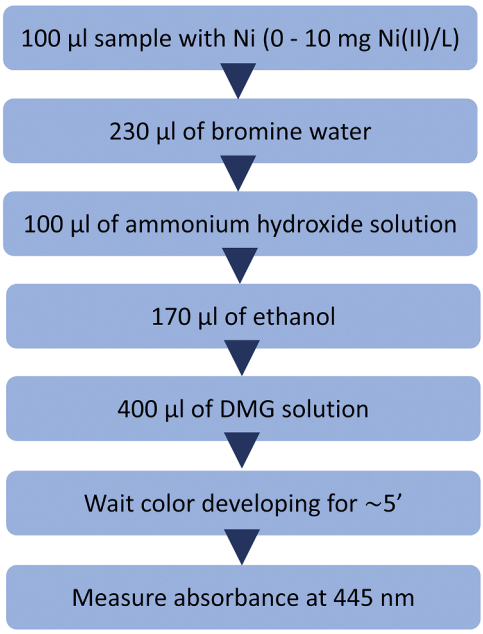

Fig. 1. General scheme procedure adopted for modified DMG protocol.

2.3. Method characterization

To determine the linearity and range of the modified method a calibration curve between 0 and 50 mg Ni(II) L^{-1} was constructed by plotting absorbance values against Ni(II) concentration. Linear regression by least square method was evaluated to check the linearity of the calibration curve. The working concentration range was determined as well as the LOD and LOQ values [23].

The LOD (Eq. (2)) and LOQ (Eq. (3)) were calculated according to the following Eq [24,25]:

$$s_0 = \frac{s_{y/x}}{A}\sqrt{1+\frac{1}{M}+\frac{x^{-2}}{\sum_{m-1}^{M}(x_m - X)^2}} \quad \text{(Eq. 1)}$$

$$LOD = 3.28S_0 \quad \text{(Eq. 2)}$$

$$LOQ = 10S_0 \quad \text{(Eq. 3)}$$

Where $S_{y/x}$= standard deviation and A = slope of the linear regression for calibration curve, M = total number of samples, $\bar{X}$ = media concentration.

All figures of merit were calculated by the software written in MATLAB 7.0. ((Mathworks, MA, USA) (MATLAB, The Mathworks, (Natick, Massachusetts, USA))) for univariate calibration, freely available on the Internet.

2.4. Color stability of Ni-DMG complex

The color stability of the complex is a decisive factor in determining a time period in which the reaction can be reliably measured. To determine the color complex stability, a sample with a concentration of 5 mg Ni(II) L^{-1} was analyzed in a spectrophotometer. Samples were measured every 3 min at 445 nm for a total time of 120 min after the addition of the DMG reagent.

Comparison between modified DMG method and AAS

The accuracy of the modified DMG method was compared with determinations done by AAS using Flame Atomic Absorption Spectrometry

(FAAS) technique. A Perkin Elmer Analyst 200 AAS from the Department of Physical Chemistry and Quality Control, Complejo Tecnológico Pilcaniyeu, Comisión Nacional de Energía Atómica was used for the determinations.

Nickel solutions of known concentrations (range 0 - 10 mg Ni(II) L^{-1}) were analyzed by both methods. Nickel concentrations determined by the DMG and AAS methods were compared and the percentage difference was calculated using the following formula [26]:

$$(ConcentrationAAS - ConcentrationDMG) * 100 / ConcentrationAAS \quad \text{(Eq. 4)}$$

Where '*Concentration AAS*' corresponds to the concentration value of the sample measured by AAS; while '*Concentration DMG*' corresponds to the concentration value of the sample measured by the modified DMG method.

2.5. Experimental samples analysis

The modified DMG method was tested with experimental samples. These samples consisted of supernatants from a nickel bioremediation assay using unicellular algae. The following algae strains (AS) were used: AS1 belongs to the genus *Coleastrum* sp., AS2 and AS5 to *Desmodesmus* sp., and AS3 and AS4 to *Chlorella* sp..

Bioremediation assays were performed as described in the literature [20,21]. Briefly, a known density of algal cells and Bold Basal Medium (BBM) [27] without EDTA, and with the addition of $NiNO_3{\cdot}6H_2O$ was incubated for 24 h. Then, samples were centrifuged, and the supernatant was analyzed. Assays were performed in triplicate with the respective controls (culture medium and nickel, without algae cells) and measured with DMG and AAS methods. Appropriate dilutions of the samples were performed prior to analysis.

2.6. Statistics

All data reported are means of triplicates ± standard deviation (SD). Statistical treatment and significant differences were analyzed using Prism 8.1 (GraphPad Software, USA). In all cases, the significance level was set at $p < 0.05$.

3. Results and discussion

3.1. Comparison of both analytical procedures: the original and the modified volume-reduced method

To illustrate the differences, a comparison between the original [11] and the modified volume-reduced method (present work) is shown in Table 1. In the modified DMG protocol, the concentrations and volumes of each reagent were precisely defined in order to improve the reproducibility of the method. In Table 1, it can be seen that the reagents used in both protocols are the same, but each volume was considerably reduced. The new protocol proposes a final volume of 1 mL, whereas the original protocol has a final volume of approximately 50 mL.

3.2. Calibration curve, linearity, LOD, and LOQ

The aim of the first experiment was to determine the linearity and the detection range of the modified method. The linearity range of the modified DMG method was up to 10 mg Ni(II) L^{-1} (Fig. 2). Changes in the slope were observed for concentrations greater than 10 mg Ni(II) L^{-1} (Fig. 2.A). The linearity range is wider than the reported in the original protocol by Mitchell et al. [11], which was between 0.1 - 5 mg Ni(II) L^{-1}. The LOQ (Eq. (2)) and LOD (Eq. (3)) obtained were 1.18 and 0.41 mg L^{-1}, respectively. These data were not reported in the original publication of the method.

Other authors, such as Riba et al. [3], used a flow-based spectrophotometric system with DMG, in which they obtained a dynamic range of 25.0 to 150 µg Ni(II) L^{-1}, with LOD and LOQ values of 6.3 and 21.1 µg Ni(II) L^{-1}. Even though this work employed DMG, the protocol as well as the concentration range are completely different from the method employed in this work. In a previous study, a concentration range of 0.50 - 5.0 mg Ni(II) L^{-1} was obtained from 1.0 mL of sample using DMG colorimetric solid phase extraction [18]. Thus, the proposed protocol for the modified DMG method falls within the range of other novel protocols which also involve optimization of standard colorimetric methods to provide simpler, cleaner and economically favorable detection methods.

3.3. Color stability of Ni-DMG complex using the modified method

Complex color stability is a critical factor to determine a range of time in which the reaction is reliable to perform measurements. The color stability of the Ni-DMG complex over time was studied (Fig. 3). The maximum absorbance was reached 6 min after the addition of DMG solution. No difference in absorbance values was measured between 6 and 20 min of the reaction (0.102 ± 0.005 absorbance). It is recommended to perform measurements between these time period to ensure accurate data acquisition.

3.4. Comparison between modified DMG and AAS methods

Dilutions of a Ni(II) stock solution in the range of 0 - 10 mg L^{-1} were analyzed by modified DMG and AAS methods. Table 2 presents the details of the quantification with both methods. The differences are expressed as percentages and statistical analysis is shown. No significant differences were found between the two methods, demonstrating the accuracy of the modified DMG method. In this sense, supplementary Figure S.1 shows a linear regression analysis indicating no differences between the two applied methods ($R^2 = 0.9991$).

The reduction of dimensions, volumes and quantities of reagents, solvents, and samples utilized is a fundamental goal in analytical chemistry [28]. The main strategy in green analytical chemistry involves miniaturization, aiming to reduce the scale of reagent

Table 1
Experimental formulation of the original and the modified protocol (this work).

Reagents	Formula	Mitchel et al. [11]		This work	
		Stock solution	Volume (mL)	Stock solution	Volume (µL)
Ni standard	$NiCl_2{\cdot}6H_2O$	0.1 - 5 mg L^{-1}	*ns; ** rp: sample of ≤0.5 mg L^{-1}	1 - 10 mg L^{-1}	100
Bromine water	$Br_{2(aq)}$	Saturated Solution (ns)	Add dropwise until solution turn yellow + 2 mL.	0.22 % m/v	230
Ammonium hydroxide	NH_4OH	Reagent quality concentrated	Add dropwise until color disappears; rp: ~10 mL	5 % v/v	100
Ethanol	C_2H_5OH	95 %	17.5 - 35 mL; rp: 35 mL	99 – 100 %	170
Dimethylglyoxime (ethanolic reagent)	$C_4H_8N_2O_2$	0.1 %	1 - 20 mL; rp: 20 mL	0.1 %	400
Deionized water	H_2O	–	Dilute to volume	–	–

* ns: not specified;.
** rp: recommended procedure.

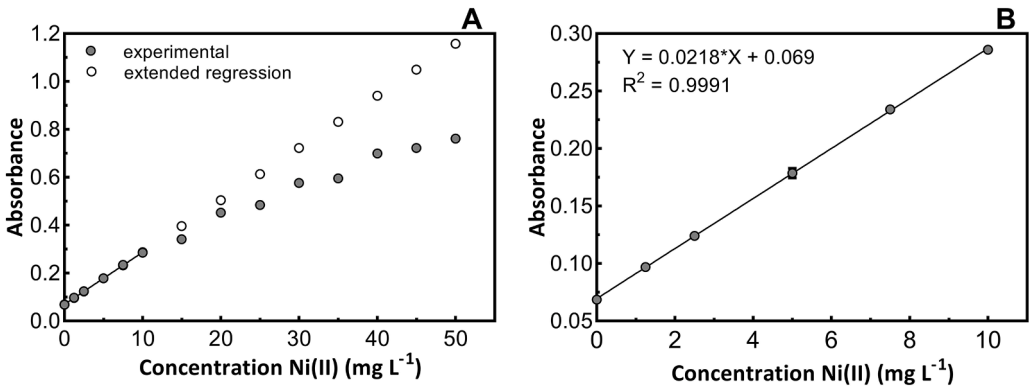

Fig. 2. **A.** Calibration curve for Ni(II) ranging between 0 - 50 mg Ni(II) L^{-1}. Black dots are the values of absorbance. White dots represent the concentration to the extended linear equation of Fig. 2.B. **B.** Calibration curve of modified DMG method ranging between 0 - 10 mg Ni(II) L^{-1}. Data are means ± SD (n = 3).

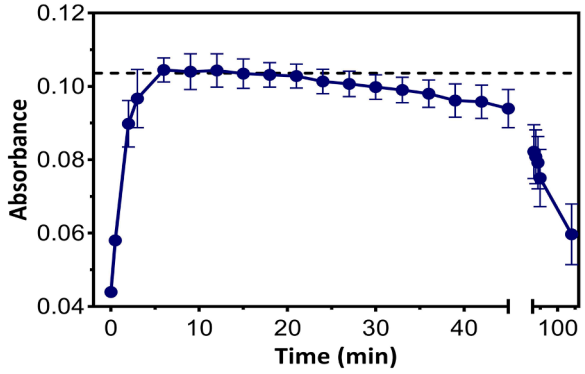

Fig. 3. Absorbance (λ = 445 nm) of 5 mg Ni(II) L^{-1} premixed with the reagents over 120 min. Data are means ± SD (n = 6).

Table 2
Comparison between nickel concentrations obtained using modified DMG and AAS methods (n = 3).

Added concentration mg Ni(II) L^{-1}	AAS		Modified DMG method			Percentage difference AAS vs DMG
	mg L^{-1}		mg L^{-1}		%	%
	Mean	SD	Mean	SD	RSD	
0	0	0	0	0	–	0.00
1.25	1.20[a]	0	1.17[a]	0.26	22.34	2.50
2.5	2.43[b]	0.05	2.40[b]	0.28	11.84	1.18
5	5.00[c]	0.1	4.84[c]	0.24	4.92	3.14
7.5	7.17[d]	0.21	7.20[d]	0.10	1.40	0.42
10	9.97[f]	0.38	9.57[f]	0.25	2.60	3.94

Equal letters represent no significant difference ($p < 0.05$) between each sample evaluated by both methods.

consumption and waste generation [29,30], and the manipulation of smaller amounts of sample volumes [12]. Numerous studies have developed techniques for determining metals with a more environmentally friendly approach [31,32].

3.5. Experimental samples analysis

An analysis was performed to evaluate the nickel concentration in experimental samples from bioremediation assays. Different algae strains were used for nickel removal as described in section 2.6.. Spectral analysis was performed between 400 and 700 nm wavelength to identify possible band shifts or additional bands near 445 and 545 nm in the experimental samples that could interfere with the DMG method measurement. It is important to analyze possible interferences because each strain has a diverse and different macromolecular composition and physiology. During the bioremediation process, algae could release different spectrophotometrically active exudates, such us polysaccharides, mucilage, or other components that could interfere with colorimetric methods [20–22].

The spectra peaks of the standard solutions of Ni(II) and the supernatant of bioremediation process with algae strains were comparable (Fig. 4). This result indicated that experimental samples did not affect the typical spectra obtained for the Ni-DMG complex. The difference in absorbance values could only be attributed to different Ni(II) concentrations in each sample.

In addition, Ni(II) determinations obtained with the modified DMG method were compared with data measured by AAS. Table 3 shows the differences between Ni(II) concentrations measured by both methods. The percentage differences (Eq. (4)) were less than 8 %. Almost all measurements were comparable with both methods, demonstrating the accuracy of the modified DMG method even for more complex samples. Only for sample AS1 there was a significant difference between the AAS and DMG results (Table 3).

4. Conclusion

In summary, a modification of the DMG method for nickel determination was successfully achieved. The process now involves only 1 mL of final volume per sample, instead of the previous 50 mL. The protocol proposed in this paper provides a fast, simple, and accurate method for Ni(II) concentration determination. Only 100 µL of sample are required to determine the nickel concentration. By placing bromine water to

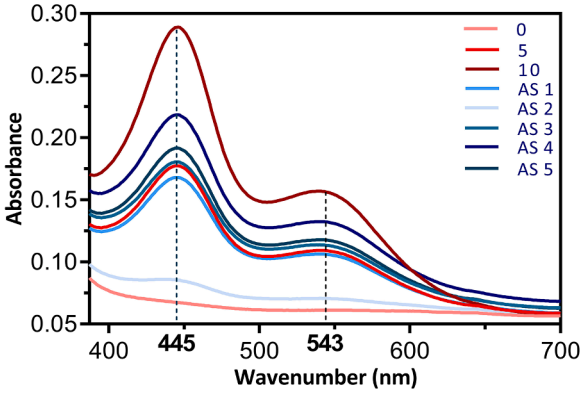

Fig. 4. Spectral responses of 0, 5, and 10 mg Ni(II) L^{-1} standard solution and Algal Strain: AS1 to AS5 experimental samples. Concentration values are shown in table 3.

Table 3
Comparison between experimental samples of various Algal Strain (AS) with different Ni(II) concentrations measure using modified DMG and AAS methods ($n = 3$).

Experimental samples	AAS		Modified DMG method			Percentage difference AAS vs DMG %
	mg Ni(II) L^{-1}		mg Ni(II) L^{-1}		%	
	Mean	SD	Mean	SD	RSD	
AS1	38.55[a]	1.20	41.57[b]	1.80	4.3	7.84
AS2	4.85[c]	1.06	4.61[c]	0.78	16.9	4.87
AS3	47.80[d]	0.14	47.02[d]	1.46	3.1	1.64
AS4	19.20[e]	0.85	18.58[e]	1.61	8.7	3.21
AS5	15.80[f]	0.00	16.04[f]	1.37	8.5	1.50

Equal letters represent no significant difference ($p < 0.05$) between each sample evaluated by both methods.

achieve complete oxidation of Ni(II) and then adding ammonium hydroxide, ethanol and DMG solution, in about 6 min the orange colored complex is obtained and measured in a spectrometer at 445 nm, to finally determine the Ni(II) concentration value. Obtained data showed a linearity range 0 - 10 mg Ni(II) L^{-1} and the LOQ and LOD were 1.18 and 0.41 mg Ni(II) L^{-1} under specific test conditions. Samples measured by the modified MGD method and the AAS reference technique showed no significant differences. We established that this protocol is suitable for a more complex matrix such as supernatants of bioremediation assays. Beyond its initial scope, this protocol can be applied to monitor contaminated water and evaluate the feasibility of effluent bioremediation processes. This reduction in volume not only simplifies the technique by reducing the amount of volumetric reagents required, but also minimizes waste, providing both economic and environmental benefits.

CRediT authorship contribution statement

Micaela B. Gómez Jousse: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Visualization. **Gisela Ferraro:** Conceptualization, Investigation, Methodology, Resources, Supervision, Visualization, Writing – review & editing. **Federico J. Pomiro:** Formal analysis, Writing – review & editing. **Daniel M. Pasquevich:** Funding acquisition, Writing – review & editing. **Carolina Bagnato:** Conceptualization, Investigation, Methodology, Resources, Supervision, Visualization, Writing – review & editing.

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.

Ethical statement

The authors have no relevant financial or non-financial interests to disclose. The authors have no competing interests to declare that are relevant to the content of this article.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtemin.2024.100130.

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