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The Potential for On-Site Determination of Mn(II) using Eco-Friendly Natural Tannins: A Cost-Effective and Sustainable Approach

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Abstract

This study exploited digital image colourimetry (DIC) with natural tannin as a reagent to determine Mn(II) in aqueous media. The calibration curve had a correlation coefficient of 0.995, indicating a strong dependence of absorbance on Mn(II) concentration. Although the spectrophotometry method with $NaIO_4$ as a reagent showed better results, the DIC method remained within an acceptable range. Both methods showed insignificant difference in measurement average and variance. Common cations in natural water interfered with Mn(II) detection at a tolerance of less than 5% except for Fe(III), which can be easily precipitated before Mn(II) analysis. The DIC method applied to three water samples showed acceptable recovery, offering an easy and inexpensive on site Mn(II) determination.

Keywords: Neurotoxic element, eco-friendly and cost-effective reagent, tannin, method validation, on the spot analysis

INTRODUCTION

Manganese (Mn) is a natural element found in rocks, soil, water, and food and is a twelfth most plentiful element in the earth's crust (Balachandran et al., 2020). Its presence in the environment also stems from human activities, such as the discharge of municipal wastewater, sewage sludge, mining and mineral processing (especially nickel), emissions from the production of ferroalloys, steel, and iron, and the burning of fossil fuels (Ali et al., 2019).

Although Mn is essential for the human body, it is also considered as a non-eco-friendly due to its neurotoxicity effect (Ruiz-Azcona et al., 2021). Therefore, its existence in the environment should be routinely monitored. However, periodic inspection of Mn in the environment is sometimes constrained by the high cost of analysis derived by use of complicated instrument such as atomic absorption spectrophotometer (AAS) (Napitupulu et al., 2019); (Kasmiati et L., 2020); (Aini et al., 2022); (Razzouk & Ali, 2021); (Megawati & Warsa, 2024); inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Razzouk & Ali, 2021); (Ola et al., 2017); (Ola et al., 2017); (Ola & Matsumoto, 2019b); (Ola & Matsumoto, 2019a); (Ola et al., 2022) spectrofluorimetric (Ahmed et al., 2018); ultraviolet-visible (UV-Vis) spectroscopy (Razzouk & Ali, 2021); (Malik et al., 2021); (Xue & Li, 2022); electroanalytical (Crapnell & Banks, 2022) etc.

UV-Vis spectrometry is favoured because it is cost-effective, versatile, and one of the simplest analytical methods for determining species concentration in liquids (Malik et al., 2021). In this method, one or more reagents are needed to react with the analyte to form a coloured compound, allowing it to be detected. The commonly used reagent is periodate which is oxidize Mn(II) to purple MnO_4^- (Razzouk & Ali, 2021). In addition, several colourful organic reagents have been proposed for determining manganese, including toluidine blue, mordant brown 33, phenoxazine, and eosin (Rustamov & Abbasova, 2014). However, periodate and recommended chromogenic reagents are not natural products and therefore are usually expensive and environmentally unfriendly. Therefore, it is critical to seek a fast and low cost but reliable technique for analysis of manganese using a cheaper and more environmental hospitable complexing agent. In this study, natural tannin extracted from *Uncaria gambir* Roxb was utilized as a complexing agent for the determination of Mn(II) ions. The tannin's ability to form complexes with Mn(II) allows for the effective measurement of

manganese concentrations through the colourimetric analysis technique. This approach exploits the natural properties of tannin, providing an eco-friendly and economical alternative for chemical analysis in environmental and industrial applications.

Tannins are a polyphenol group with high molecular weights that can be found in the bark, wood, leaves and fruits of a variety of plants species (Das et al., 2020); (Dikatoru et al., 2024). Because tannins have the tendency to form complexes with different transition elements (Koopmann et al., 2020), it can also be used as a complexing agent for Mn(II). By using tannin as complexing agent, the disadvantages derived by the using of conventional reagents can be solved as it can be easily extracted from the plant tissue using the low-cost solvents where water is the most commonly used with the simple method such as maceration (Istyami et al., 2024); (Taufiq & Sulfiani, 2023). Furthermore, because tannins are extracted from the plant tissues, they should not be an environmental xenobiotic.

In previous work, tannin has also been used as a reagent to determine Mn(II) using an analytical device based on microfluidic paper (μ-PAD) method integrated with a smart phone (Nitti et al., 2023). However, the μ-PAD method required an additional stage called the fabrication of μ-PAD, where the success of this technique is highly dependent on this stage. Even worse, the preparation of the μ-PAD was the hardest step and therefore needed to be performed by a conversant person, which limits its application. A simpler technique is needed to allow less skilled people to execute the analysis in order to facilitate Mn(II) determination.

Digital image colorimetry **(**DIC**),** a technique that involves digitizing images taken by devices like mobile phones, digital cameras, webcams, scanners, and similar tools, can be used to simplify the μ-PAD method (James & Honeychurch, 2024). By using the DIC method, the step of μ-PAD preparation can be removed from the analysis procedure. This article presents a study on the use of DIC for the determination of manganese (Mn(II)) ions in aqueous media, employing natural tannins as a green and cost-effective complexing agent. This method can serve as an alternative to traditional spectrophotometric techniques for Mn(II) detection, with the advantage that samples can be analyzed instantly at the sampling site. This eliminates the need for transport to a laboratory, which can cause degradation, deteorioration, and contamination. Additionally, the analysis can be performed by less experienced individuals.

METHODOLOGY

Materials and Instrumentals

Tannin extracted from the leaves and twigs of *Uncaria gambir* Roxb was supplied by CV Kempan Kab. Lima Puluh Kota, Indonesia and was certified by Center of Industrial Research and Standardization, Padang, Indonesia with tannin content of 27.76 % (b/b). $MnSO_4$, methanol, HCl, $NaIO_4$, CH_3COOH, CH_3COONa and HNO_3 were all in analytical grade and were supplied by Merck. All chemicals, including tannin, were used without additional purification. All aqueous solutions in these experiments were prepared using de-ionized water supplied by PT Brataco (Indonesia).

Determination of optimum conditions

Based on the absorption spectra of natural tannin mixed with Mn(II) (Figure 1(b)), it is hypothesized that a new compound has been formed between them. Therefore, it was necessary to find the optimum conditions for the formation of this compound including pH, ratio, and stable time.

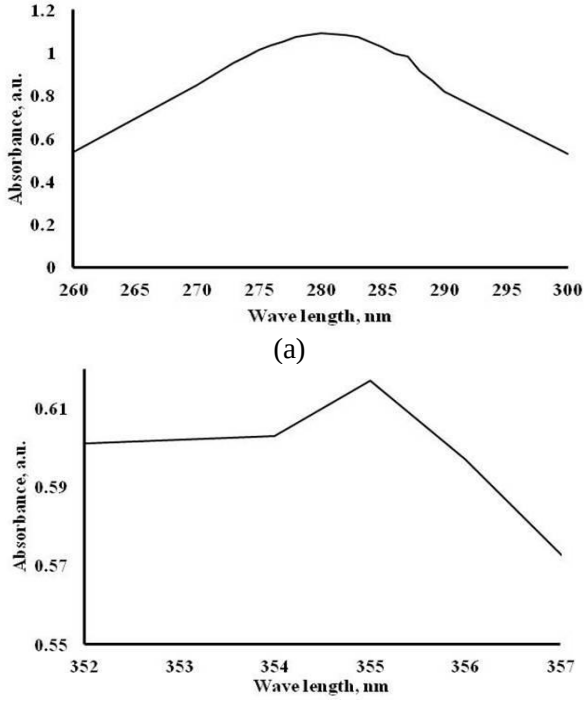


Figure 1. Absorption spectra of tannin (a) and its mixture with Mn(II) (b)

The determination of those parameters was conducted by modifying the procedure proposed by Zhang et al. (Zhang et al., 2016) as follows: 2.5 mL of tannin 100 mg/L (dissolved in methanol 50 %) and 21.5 mL of acetate buffer solution, prepared by mixing of specific volumes of 0.1 mol/L nitric acid, 0.1 mol/L acetic acid and 0.1 mol/L sodium acetate,

were combined. Into the mixture, 1.0 mL of Mn(II) salt of 1.0 mmol/L (dissolved in HCl 0.1 mol/L) was added and the absorbance of the mixture was recorded using a visible spectrophotometer (Shimadzu UV-Vis spectrophotometer UV-1780).

Determination of Analytical Performance Parameters

Based on the obtained optimum conditions, a series of standard solutions of Mn(II) was prepared. The DIC method was employed to obtain the reflectance of those standard soluitions with the aid of a homemade box, as shown in Figure 2.

Figure 2. Homemade box for taking photo of samples

The detailed procedure for DIC method referred to Tambaru (Tambaru et al., 2018) as follows: each standard solution was positioned at the bottom-centre of the box, which had a 30-watt Visicom LED bulb lamp fixed at the top-centre to ensure consistent lighting conditions during image capture. A 13 MP camera on a Vivo V20S smart-phone was used to take pictures of the solution through the box's 4 x 4 cm window, with a 9 cm distance between the camera and the sample, producing in the images. The RGB viewer software was utilized to change the images into colour intensities of Red, Green, and Blue (RGB), which were then converted into reflectance, R of each solution using Birch and Stickle method using equation (1) (Shishkin et al., 2004).

$$R = -\log \frac{I}{I_0} \quad (1)$$

where I represent the mean red colour intensity of each standard solution or sample soltuion, I_0 indicates the mean red blue colour of the blank solution which had the same composition as the standard solution, except it did not contain Mn(II). A calibration curve was plotted using the obtained reflectance from which performance parameters such as correlation coefficient (r), sensitivity, limit of detection (LoD), and limit of quantitation (LoQ) can be assessed. The other analytical performance parameters viz error (%E), recovery (%R) and relative standard deviation (%RSD) can be estimated by repeated measurement of six standard solution of Mn(II) with a certain concentration. As a reference standard method, an UV-Vis spectrophotometer with $NaIO_4$ as an oxidizing agent was also employed in the evaluation of those parameters.

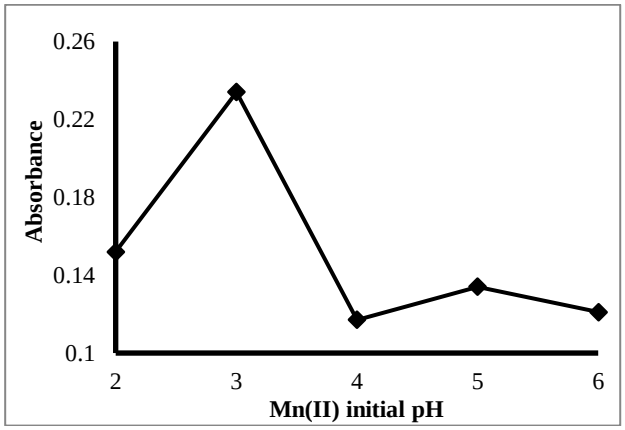
Interferences Study

To apply tannin as a complexing agent in analysing of Mn(II)-contained real water samples, it is critical to study the effect of common ions found in water including Na^+, Mg^{2+}, Ca^{2+}, and Fe^{3+}. The effect of thouse cations on the determination of Mn(II) was investigated individualy by introducing the interfering cations in the determinations of Mn(II). The reflectance was measured using the DIC method both with and without the presence of interfering ions. The tolerable limit was defined as the concentration of interfering ions that caused a 5% error in the determination of Mn(II).

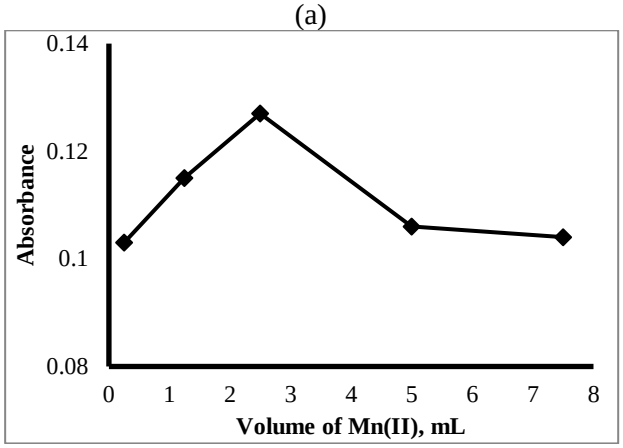
RESULTS AND DISCUSSION

Optimum Conditions for Mn(II) –Tannin Reaction

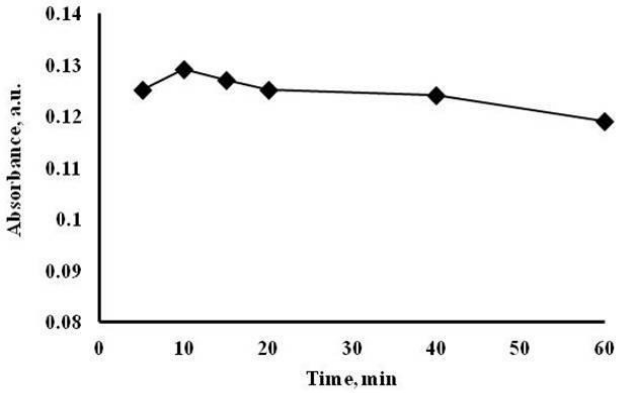
Based on the spectra shown in Figure 1(a), the tannin was probably condensed tannins. This type of tannin present a strong absorption around 200 nm with λ_{max} between 279-281 nm (Falcão & Araújo, 2013). Because tannin is a hydroxyl-rich group of natural product, its reaction with metal ion including Mn(II) is absolutely affected by the solution pH and their reaction probably produce a chelate compound. Theoretically, the –OH group will be protonated at the lower pH and will be deprotonated at the higher pH. As a consequence, the highest concentration of the chelate tannin-Mn(II) was only observed at a certain pH, represented by the mixture absorbencies. The absorbances of mixture at various pH of mixture were recorded at 355 nm (λ_{max} of tannin-Mn(II) as shown in Figure 1(b)) and is shown in the Figure 3(a).



(a)



(b)



(c)

Figure 3. Optimum condition of the tannin-Mn(II) mixture including pH (a), ratio (b), and stability time (c)

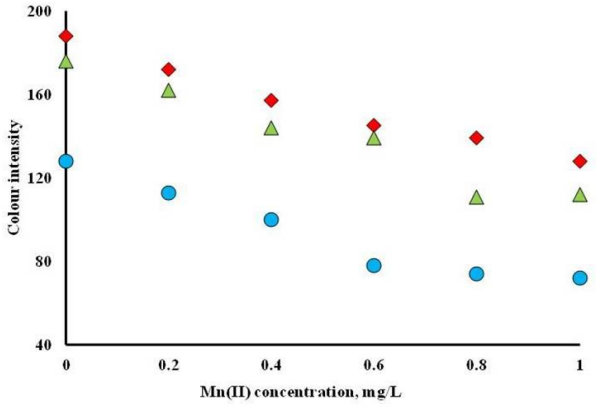
The curve in the Figure 3(a) shows that the highest absorbance was observed at pH 3 which means that at this pH, the most stable of tannin-Mn(II) complex was obtained. At the lower pH the H^+ ion disturbed the stability of chelate, similarly at the higher pH, the OH^- probably react with Mn(II) to form $Mn(OH)_2$. Both occurrences lowering the concentration of the chelate which in turn decreased the absorbance of the mixture. This optimum pH was then used to investigate the optimum ratio of tannin-Mn(II). At low concentrations of tannin some of Mn(II) do not react with tannin to produce colour, while too high of its quantity perhaps interfere the colour measurement because tannin itself is also coloured. Amount 2.5 mL of tannin (100 mg/L) was mixed with various volume of Mn(II) 55 mg/L, diluted to 25 mL using buffer solution pH 3 and the absorbance of each solution was measured as shown in Figure 3(b).

Result shows that optimum volume ratio was achieved when 2.5 mL of Mn(II) was added which means that at this point 1 mg/L of Mn(II) required about 1.82 mg/L of tannin to make a complete reaction. After optimum ratio, the stability of the chelate was presumably disturbed by the excess of HCl used as a solvent for preparation of Mn(II) solution. These two optimum conditions were then used to evaluate the stable time of the mixture such as shown in Figure 3(c). Figure 3(c) shows that the stability of chelate decreased with time where the stability dropping was relatively high after 40 minutes. Therefore, the photos capturing was carried out before 40 minutes in the further experiments.

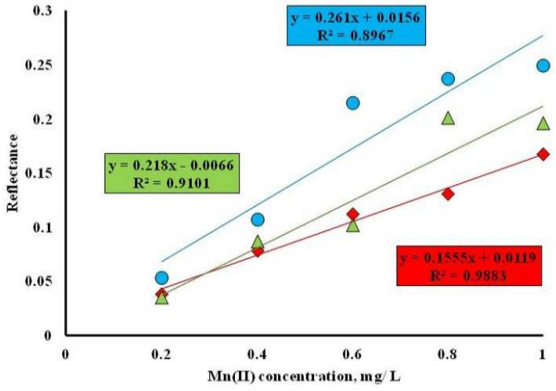
Analytical Performance Parameters

To verify the performance of an analytical method, it is critical to plot a calibration curve based on the concentration ratio of Mn(II) to tannin previously obtained. According to the history of analysis using atomic absorption spectrophotometry, the concentration of Mn(II) in manganese-contained wastewater was 0.131± 0.002 mg/L. Therefore, a series of Mn(II) standard solution with maximum concentration of 1 mg/L was prepared. Each standard solution was put into the homemade box (Figure 2) and the photo was captured. The images produced were analysed for colour intensity using RGB viewer software, resulting in colour intensities like those shown in Figure 4(a). By applying the equation (1), these colour intensities were converted to reflectance values, which were then used to create the calibration curve shown in Figure 4(b). Colour intensity (Figure 4(a)) and calibration curve (Figure 4(b)), indicated that the highest intensity and linearity was shown by red component. Therefore, the red component was applied both in the estimation of analytical performance parameters, and in the further experiment. As a standard reference method, Mn(II) calibration curve was also plotted using the UV-Vis spectrophotometry method with $NaIO_4$ as an oxidizing agent such as shown in the Figure 4(c). In order to evaluate the reproducibility of the method, and to compare it with a standard reference method, 6

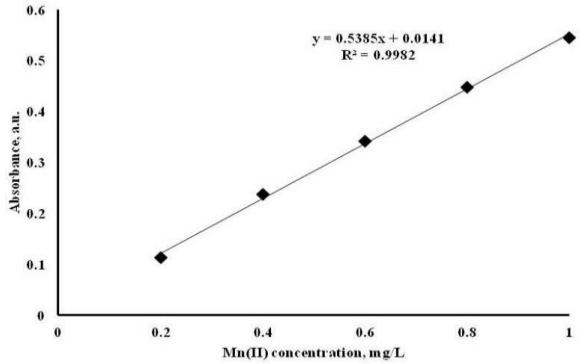
sample solutions of 0.800 mg/L Mn(II) were analysed using both DIC method and spectrophotometry method, and its result is indicated in the Table 1. By using Figure 4(b), 4(c), and Table 1, analytical performance of several parameters has been estimated such as displayed in the Table 2.



(a)



(b)



(c)

Figure 4. Colour intensity (a) and calibration curve of Mn(II) using DIC method with tannin as reagent (b), and spectrophotometric method with $NaIO_4$ as reagents (c)

Table 1. Measured concentration of Mn(II) 0.800 mg/L using DIC and spectrophotometry method(SM)

Solution number	Mn(II) concentration, mg/L	
	DIC	SM
1	0.831	0.814
2	0.800	0.809
3	0.800	0.799
4	0.831	0.803
5	0.812	0.820
6	0.831	0.816
Average	0.8175	0.8101
SD	0.015424	0.007335

Table 2. Analytical parameters comparison of the DIC and the spectrophotometry method (SM)

Parameters	Estimation formulas	Methods	Result
Error (%E)	$\%E = [\frac{\bar{X}-\mu}{\mu}]$ x 100%	SM DIC	1.2625 2.1875
Recovery (%R)	$\%R = \frac{\bar{X}}{\mu}\ x\ 100\%$	SM DIC	101.2625 102.1875
Relative Standard Deviation (%RSD)	$\%RSD = [\frac{SD}{\bar{X}}]$ x 100%	SM DIC	0.9054 1.8867
Limit of Detection, LoD (mg/L)	$LoD = \frac{3S_Y}{S}$	SM DIC	0.0466 0.1193
Limit of Quantitation, LoQ (mg/L)	$LoQ = \frac{10S_Y}{S}$	SM DIC	0.1553 0.3976
Sensitivity	Reflected from the curve's slope value	SM DIC	0.5159 0.2133
Correlation coefficient (r)	$r = \sqrt[2]{R^2}$	SM DIC	0.9991 0.9941
t-calculated	$t_{calc.} = \left\| \frac{X_1 - X_2}{S_{pooled}\sqrt{\frac{1}{n_1}+\frac{1}{n_2}}} \right\|$	1.0587	$t_{calc.} < t_{critical}$
t-critical (95 %)		2.2281	
F-calculated	$F_{calc.} = \frac{SD_1}{SD_2}$, $SD_1 > SD_2$	2.1028	$F_{calc.} < F_{critical}$
F-critical (95 %)		5.0503	

$\bar{X}$ represent the Mn(II) average concentration, μ is the true concentration of Mn(II), SD is the standard deviation, S_Y reflect the standard error of the curve intercept, S is the slope of the curve, S_{pooled} is the combination of SD_1 and SD_2 formulated as $S^2_{pooled} = \frac{(n_1-1)SD_1^2+(n_2-1)SD_2^2}{(n_1+n_2-2)}$, where SD_1 and SD_2 are the standard deviation of DIC and SM method, respectively, n_1 and n_2 are the number of measurement for DIC and SM method, respectively.

Table 2 indicate that for all parameters, spectrophotometry method with $NaIO_4$ as a reagent exhibit the better result compared to that of DIC method. However, the results of DIC method are still in the range of acceptable. In case of %R and %RSD, according to Latimer (Latimer et al., 2023), for the analyte concentration of 0.1 % (0.8 mg/L in this work

is equal to ± 0.00008%) are 80-110% and 7.3%, respectively. The correlation coefficient (r) of the proposed method was 0.9941, indicating a strong dependence of reflectance to the concentration of Mn(II) complexed with natural tannin. The LoQ of the DIC method was 0.3976 mg/L, which falls within the acceptable concentration range of Mn(II) in drinking and clean water as specified by the Indonesian Ministry of Health Regulation Number 492/MENKES/PER/IV/2010 of 0.4 mg/L. This implies that the proposed method can be applied for the analysis of Mn(II) in drinking and clean water.

Interferences Study

One of the characteristics of the chemical analysis in the laboratory level is the inexistence of the interferences. If an analytical method is un-free from the influence of possible interferences all other performance parameters become less reliable (Verbić et al., 2013). Due to the nature of tannins that is able to react with all cations, it is critical to assess the determination selectivity of Mn(II) against other cations that potentially compete with Mn(II) to react with tannins. In this study, the focus was on the most prevalent cations found in environmental waters, including Na^+, Mg^{2+}, Ca^{2+}, and Fe^{3+}. At a molar ratio of 1 : 1, the effect of interference cations on the reflectance of complex tannin-Mn(II) is displayed on Table 3.

Table 3. Level of interference cations in the molar ratio of 1:1

Interfering cations (salt)	Interference level (%)
Na^+	1.0
Mg^{2+}	3.5
Ca^{2+}	4.6
Fe^{3+}	229

The results in Table 3 indicated that the highest interference was shown by the Fe(III) cation, which is consistent with the μ-PAD method coupled with a smart-phone (Nitti et al., 2023). This interference will cause a significant deviation when applying this method to analyse Mn(II) in a sample that also contains Fe(III). To minimize this interference, it is absolutely necessary to remove Fe(III) from the sample solution prior to Mn(II) determination. It was recommended that the adding of 0.5 M orthophosphate to the sample could presipitate Fe(III) as $Fe_3(PO_4)_2$ (Zhang et al., 2011). In comparison with the μ-PAD method, the proposed method exhibited higher interference. However, this method is superior in terms of convenience because it did not require the preparation of μ-PADs, which is a critical step for the success of Mn(II) analysis with natural tannin as a complexing agent but is unnecessary in the DIC method.

Analysis of Real Water Samples

Analysis of real water samples containing Mn(II) was conducted to evaluate the effect of the sample matrix on the recovery of the analysis. Owing to the Mn(II) concentration in the three selected samples being lower than the LoD and LoQ of the proposed method, it was necessary to add the Mn(II) standard to the samples to increase the concentration, ensuring that the measurement results meet the acceptance criteria for precision and accuracy. The analysis was carried out in triplicate, as shown in Table 4. According to Latimer (Latimer et al., 2023), the recoveries of Mn(II) in all analysed samples were within the acceptable range.

Table 4. Application of DIC Method for Analysis of Mn(II) in selected water samples

Samples	pH	Mn(II) concentration, mg/L			Recovery (%)
		Initial[b)]	Added	Found	
Tap water (Kupang city)	7.01 ± 0.02	0.064 ± 0.002	0.000	0.020 ± 0.003	-
			0.600	0.684 ± 0.006	103.30
			1.000	1.062 ± 0.032	99.80
Well water (Kupang city)	7.14 ± 0.01	0.083 ± 0.003	0.000	0.008 ± 0.032	-
			0.600	0.666 ± 0.010	100.10
			1.000	1.044 ± 0.007	97.90
Mn processing waste water[a)]	6.90 ± 0.02	0.101 ± 0.002	0.000	0.093 ± 0.003	-
			0.600	0.703 ± 0.002	100.33
			1.000	1.087 ± 0.003	98.60

[a)]From the waste storage of PT Anugerah Nusantara Sejahtera, located in the district of Timor Tengah Utara, Indonesia, [b)] measured using UV-Vis spectrophotometry with $NaIO_4$ as the reagent.

CONCLUSION

This study demonstrated that natural tannin from *Uncaria gambir* Roxb can be used as a cost-effective and environmentally friendly reagent to determine Mn(II) in aqueous media in a simple manner. The proposed DIC method can be conducted using a homemade box and a smartphone camera. Results

show a strong correlation (r= 0.994) between the Mn(II) concentration complexed with natural tannin and absorbance. Comparison of the proposed method with a standard reference method showed that the standard reference method gave better results for all evaluated parameters. However, the results from the DIC method were still within an acceptable range, and a statistical assessment showed that these two methods were not significantly different in terms of measured average Mn(II) concentration and variance. Common cations in natural water interfere with Mn(II) determination at a tolerance of less than 5%, except for Fe(III), which can be easily precipitated before Mn(II) analysis. Application of the DIC method to determine Mn(II) in three water samples showed that the measurement recovery fell within an acceptable range.

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