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# Colorimetric-Based Concentration Measurement of Manganese Ions using Spectroscopy Approach

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## ABSTRACT

*This paper presents the spectroscopy analysis of manganese ions ($Mn^{2+}$) to investigate the correlation between its concentration and optical absorbance at different wavelength spectra. This work was performed as a preliminary work to establish guidelines and references for future work in developing a monochromatic light-based colorimetric system for concentration measurement of $Mn^{2+}$. The samples were prepared at the concentration range of 0.2–1.0 ppm using a colorimetric reagent (i.e., 0.1 % PAN solution) that produced an orange-based coloured solution. Qualitative analysis was performed to obtain the absorbance spectra, which are significant in identifying the suitable colour of monochromatic light (e.g., LED), as well as to predict the settling time for steady-state condition before the measurement could be taken. The results showed that for the range of concentration studied, the blue to cyan region gives the best absorbance with peak absorbance wavelength occurred at around 495 nm. Testing at the time interval between 30 and 90 min after sample preparation also gives the indication of the steady-state condition for a complete colorimetric reaction. Then, quantitative analysis was performed to obtain a standard calibration curve that relates optical absorbance and $Mn^{2+}$ concentration.*

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*The curve is significant to serve as a standard reference for the results to be obtained during colorimetric system development. The calibration curve gives a good linearity at $R^2 = 0.99$, thus verifying the sample preparation and measurement procedures, as well as instrumentation setting used in this work.*

*Keywords: Colorimetric; manganese ion; optical absorbance; spectroscopy*

## INTRODUCTION

Heavy metals are elements that exist naturally and can be produced from various human activities. One of the global concerns is the influence of heavy metals towards the quality of water, which can give several implications in the case of excessive intake [1]. It is reported that heavy metal ions could be originated from various sources with adverse health effect [2]. Among these ions, manganese is one of the important substances that can reside in our domestic water supply systems and can be consumed through drinking water and food [3]. Living in a contaminated environment also becomes a factor for excessive exposure to such metal elements [4]. In human body, manganese ions ($Mn^{2+}$) are required as a cofactor for a great number of enzymes with many functions [5]. $Mn^{2+}$ is also considered as an essential nutrient for a variety of metabolic functions [6] with the capability of improving our immune system through the incorporation of the metal into metalloproteins [7]. However, excessive concentration level of this metal ion could be harmful and bring negative effect to human health. Different limits of $Mn^{2+}$ concentration have been reported as threshold levels for safe intake of the ions, especially through drinking water supplies [8,9]. Therefore, the detection of $Mn^{2+}$ is an important task to ensure that early detection and proper measures could be taken to prevent any unwanted situation [10,11]. In general, different methods are used to detect and measure heavy metal ions, including $Mn^{2+}$. Spectroscopy is the most common method implemented for this purpose with the use of commercial instruments, such as inductively coupled plasmaoptical emission spectrometry (ICP-OES) and ultraviolet-visible (UV-Vis) spectrometry, which operate based on absorbance and colorimetric principles [12-15]. In colorimetry, optical wavelength and reaction time are among the crucial parameters affecting detection performance [16]. The use of alternative instruments, such as scanometry is also possible to detect specific metal ions in several water sources [17]. However, the use of those techniques is still restricted to several issues, such as high cost and only limited to laboratory use. Therefore, there is a crucial need for a similar system that has low-cost implementation with the capability to be expanded to real-time and in-situ application [18,19]. The system should also be suitable for the deployment in early warning activity to replace traditional methods [20]. In order to develop such system, a preliminary work needs to be performed to identify several criteria required for such development, thus becoming the motivation of this work. The aim of this paper is to use a spectroscopy technique to investigate suitable wavelength and appropriate/suitable settling time for the steady-state condition of colorimetric reaction, and also to obtain a calibration curve that relates optical absorbance to $Mn^{2+}$ concentration. The finding is significant as a guide and reference in the future development of a low-cost colorimeter system that uses monochromatic light (e.g., LED) as an optical source. In this work, the aim is to obtain a linear calibration curve that will indirectly verify the sampling and treatment methods used for this preliminary work. The same sampling procedure is then used in order to verify the system to be developed in the future.

## MATERIALS AND METHODS

Spectroscopy technique was selected as the method to determine the relationship between optical absorbance and $Mn^{2+}$ concentration based on colorimetric effect. A spectrometer (HACH DR2800) was used to conduct the qualitative and quantitative tasks. The spectrometer has the advantages of portability with a small footprint, an intuitive touch screen user interface, and accommodates a wide range of pre-programmed water analysis methods.

### A. Chemicals, reagents, and samples preparation

Specific chemicals and reagents were used for preparing the solutions containing $Mn^{2+}$ at different concentrations. The chemicals used were manganese (II) sulphate ($MnSO_4$), ascorbic acid powder pillow, alkaline cyanide reagent, and 0.1 % PAN indicator solution. $MnSO_4$ in powder form was used as $Mn^{2+}$ sources. PAN indicator solution is a colorimetric reagent used to induce colour changes in the presence of $Mn^{2+}$ in the sample.

Ascorbic acid and alkaline cyanide reagents were used for reducing the high oxidation state of manganese within the sample to the lowest oxidation state of +2 and masking all interferences by other metals. In general, the samples were prepared through several titration and dilution procedures. First, a stock solution was prepared by initially weighing a specific amount of $MnSO_4$ powder, depending on the concentration of interest using an analytical balance. Then, distilled water was added into a beaker containing MnSO4 powder to form the stock solution. Based on the standard formula and sample preparation procedures, a suitable amount of $Mn^{2+}$ solution was pipetted and diluted to form solutions with the concentration of interest. Then, several drops of ascorbic acid and alkaline cyanide were added into the test cells consisting solutions with different concentrations and swirled gently. Finally, several drops of 0.1 % PAN indicator solution were added and swirled again to form colorimetric assay solutions.

## B. Qualitative analysis (Wavelength scan)

For qualitative analysis, wavelength scanning was performed to investigate the absorbance effect of different wavelengths of light at specific concentrations of solutions under test. The wavelength was set at the range of visible light between 400 and 700 nm.

### i. Blank and 1 ppm $Mn^{2+}$ concentration solution

In this task, the aim is to observe the absorbance characteristics between the blank solution (without $Mn^{2+}$) and 1 ppm solution (with $Mn^{2+}$). 1 ppm solution is the highest concentrated $Mn^{2+}$ used as the sample in this work. Both samples were prepared according to the outlined procedures and tested after 30 minutes time interval after preparation with the assumption that complete colorimetric reaction has occurred. The absorbance spectra of these two solutions were obtained from the spectrometer reading. In this analysis, the blank solution is expected to give the minimum absorbance value, which is considered as a baseline value. Meanwhile, the 1 ppm solution (with $Mn^{2+}$) is expected to give the maximum absorbance value. The finding from this test is important for two reasons. The first reason is to identify the peak wavelength and the colour region for the purpose of selecting suitable LED colour for future monochromatic colorimeter design. The second reason is to observe the difference of absorbance between the blank solution (without

$Mn^{2+}$) and 1 ppm solution (with $Mn^{2+}$) at this colour region. It is significant to identify the difference of absorbance between the minimum/baseline and maximum values of several selected wavelengths within the same colour region to predict the span of measurement and potential variation that could arise in the case of different wavelength of monochromatic light source is selected in our future colorimeter development.

### ii. 1 ppm $Mn^{2+}$ solution at different testing time intervals

In this task, the aim is to determine the sufficient time taken for complete colorimetric reaction to occur before the absorbance measurement is taken. The significance of obtaining this sufficient reaction time is to ensure the peak wavelength is obtained at its stable state condition after reaction. If the test is performed at its transient time, the measurement could be inaccurate due to incomplete chemical reaction between $Mn^{2+}$ and the colorimetric reagent. On the other hand, if the samples are tested beyond this sufficient time, the quality of the samples might have degradation issue, which also leads to inaccurate measurement. The experiment was performed by initially preparing several samples at the concentration of 1 ppm. Then, the wavelength scan was performed at several time intervals after the preparation of the samples (i.e., 5, 30, 60, 90, and 120 min) by assuming that other parameters, such as pH and temperature of the sampling process, are maintained. The peak wavelength of every sample was identified and plotted against these intervals to observe its behaviour. Sufficient time interval is important to estimate the required time interval to test the samples by using the monochromatic light-based colorimeter to be developed in our future work.

## C. Quantitative analysis (Absorbance against concentration)

The objective of this experiment is to obtain a calibration curve that represents the relationship between the absorbance and concentration of $Mn^{2+}$. The curve was used to quantify the unknown concentration of $Mn^{2+}$ based on the absorbance characteristics. In this experiment, the monochromatic wavelength found from qualitative work was used as a light source with the assumption that other parameters, such as room temperature and pH, are fixed to ensure the experiment was performed under a controlled environment. The only manipulated variable is the concentration of $Mn^{2+}$.

Based on the preparation method highlighted above, a set of $Mn^{2+}$ ions was prepared at the concentrations of 0.2, 0.4, 0.6, 0.8, and 1.0 ppm.

### i. Linearity of calibration curve

In order to minimise the sampling error that could originate from the preparation process, an average of five sets of measurement was taken. Then, the calibration curve that represents the relationship between absorbance and concentration was plotted to study the absorbance behaviour of $Mn^{2+}$ at different concentrations. The linearity of the calibration curve was determined using the coefficient of correlation ($R^2$) obtained from the graph. The standard deviation ($\sigma^2$) of each measurement was also computed to determine the deviation of absorbance measurement for five different sets of samples. The standard deviation also represents the procedure error that might lead to systematic error, which can be used to validate the procedure used for the sampling process. It is expected that the used procedure will give small values of $\sigma^2$ as the same preparation method is to be used in our future work. The values also indicate the reproducibility of the experiment under the same conditions. In the context of an experiment, reproducibility measures whether an entire study or experiment can be reproduced in its entirety.

### ii. Repeatability of measurement

One of the important performance criteria that needs to be considered is the repeatability of measurement for the same set of samples. Repeatability measures the variation in measurement taken by a single instrument or person under the same conditions. This parameter was obtained by repeating the measurement after completing one measurement cycle (i.e., using the same sample). The process was repeated for three times and the graph of absorbance against concentration of $Mn^{2+}$ was plotted to observe the distribution of the data. For the measurement set, $\sigma^2$ was calculated to predict the possible error for the same set of samples. The test aims to identify the instrumental error that might also contribute to the systematic error. In this experiment, it is also expected that the repeatability test gives a small deviation error in order to verify the reliability of the instrument and technical setting used for the measurement.

## RESULT AND DISCUSSION

### A. Sample preparation

Figure 1 shows a set of samples containing different concentrations of manganese. The addition of a colorimetric agent (0.1 % PAN indicator solution) gives specific colour to the solutions with and without $Mn^{2+}$ ions.

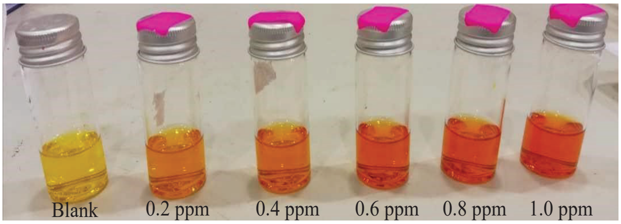

**Figure 1: Colorimetric assays of manganese at different concentrations**

The transition from yellow (i.e., blank solution) to orange colour was observed for all five samples containing $Mn^{2+}$. The light orange colour was observed for a low concentration of manganese whereas the dark orange colour was observed for a high concentration of manganese. The higher the concentration of manganese in the sample, the darker its orange colour.

### B. Qualitative analysis (Wavelength scan)

#### i. Blank and 1 ppm $Mn^{2+}$ concentration solutions

Figure 2 shows the absorbance spectra of both blank and 1 ppm $Mn^{2+}$ solutions. Both spectra showed a quite similar trend of varying absorbance throughout the range of the tested wavelength. In general, the absorbance increased until it reached the maximum before the absorbance started to decrease. At the peak wavelength, the absorbance is maximum, indicating that the samples under test absorb maximum light at that particular wavelength. In monochromatic light colorimeter design, the selection of wavelength with maximum absorbance is significant to increase the sensitivity of detection and to reduce any potential interferences.

From the figure, it is observed that the peak wavelength for both solutions is different, due to the fact that different colour solutions have different absorbance behaviour at different wavelengths (i.e., peak absorbance of blank solution occurs at 478 nm whereas peak absorbance of manganese solution occurs at 495 nm). If a monochromatic light source is to be implemented, the use of any wavelength that lies between 460 and 500 nm to measure the concentration of $Mn^{2+}$ is considered to be suitable due to high absorbance behaviour. Based on the general relationship between wavelength and colour, these wavelengths correspond to the blue to cyan colour region, which is useful in selecting the right colour of monochromatic light, such as LED.

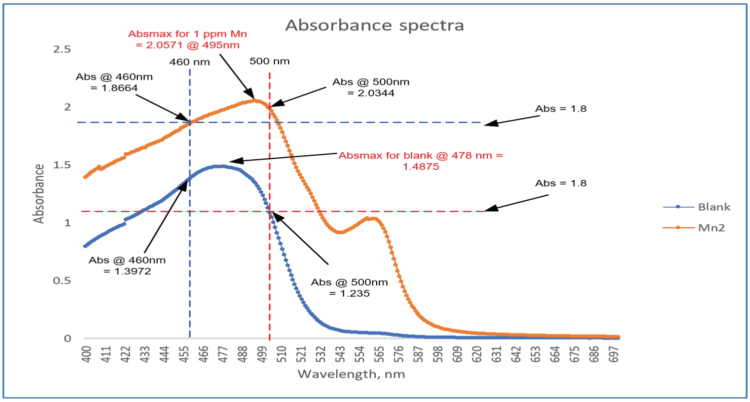

**Figure 2: Absorbance spectra of blank (solvent only) and sample (solvent with $Mn^{2+}$) solutions**

On the other hand, the difference of absorbance between blank (i.e., the lowest concentration) and $Mn^{2+}$ sample solutions (i.e., the highest concentration) also gives an indication that the absorbance effect is capable of producing a corresponding signal that can differentiate solutions with different concentrations between these two reference points. However, for monochromatic light source design, the existence of two different peak wavelengths for the baseline and 1 ppm solutions could lead to the design conflict in determining the best suitable wavelength. Therefore, by focusing on the blue to cyan region, the analysis is extended by studying the gap of absorbance at five different wavelengths (within the blue to cyan region obtained from Figure 2) to predict the possible variation in span measurement for monochromatic wavelength implementation at the selected colour region. Table 1 shows the difference in absorbance between the blank solution (baseline) and manganese solution (1 ppm) at five selected wavelengths (in blue region), which are extracted from Figure 2.

**Table 1: Absorbance difference between the minimum (baseline) and maximum concentrations for the selected range of wavelength (blue to cyan region)**

| Wavelength (nm) | Absorbance (Blank) | Absorbance (1 ppm sample) | Absorbance Difference |
|---|---|---|---|
| 460 | 1.3972 | 1.8664 | 0.4692 |
| 470 | 1.4754 | 1.9366 | 0.4612 |
| 480 | 1.4807 | 1.9869 | 0.5062 |
| 490 | 1.4258 | 2.0358 | 0.6100 |
| 500 | 1.2350 | 2.0344 | 0.7994 |

It shows that the high gaps or differences of absorbance occur at the wavelength approaching cyan colour (490 to 500 nm). Theoretically, by selecting the monochromatic light source at these wavelengths, the maximum span of measurement can be obtained for the range of concentration under test. The largest span is required for better sensitivity of the developed system. However, the usage of a monochromatic light source such as LED with such wavelength is still subjected to its availability due to various issues in LED manufacturing. In finding the exact wavelength, there might be some difficulties as commercial LEDs are normally available in RGB colour. There are also cases where the manufacturers sometimes overclaim the wavelength specification of their product or the components are sometimes mislabelled in terms of its wavelength. In this case, the use of wavelength close to the optimum wavelength is still possible but lower absorbance characteristics should be expected.

### ii. 1 ppm $Mn^{2+}$ solution at different reaction times

Table 2 presents the peak wavelength obtained for the colorimetric samples (i.e., at 1 ppm) tested at different times after being prepared using the standard procedures. The interest of this specific work is only to observe the sufficient gap between the preparation and test periods once the samples are prepared. It is observed that there are possibilities of having different peak measurement values at different periods of testing after the preparation of samples.

**Table 2: Peak wavelength of 1 ppm of $Mn^{2+}$ samples at different testing time intervals**

| Time (min) | Maximum Wavelength, $\lambda_{max}$ (nm) |
|---|---|
| 1 | 467 |
| 30 | 495 |
| 60 | 495 |
| 90 | 495 |
| 120 | 493 |

The peak wavelength was observed at 467 nm by testing at the gap of 1 min after preparation. At this time, it is considered that the measurement is still in its transient time due to incomplete colorimetric chemical reaction. Consequently, when the tests were performed after 30–90 min of preparation period, stable measurements were observed and consistent at 495 nm throughout these periods. These periods are to be used as a guide in colorimeter development in the future to verify measurement. The peak wavelength begins to display a declining pattern after 120 min. After this interval, it is assumed that the sample's quality starts to degrade. Thus, the pattern suggests that the sample should have sufficient time to allow the completion of colorimetric reaction. However, these findings still require more experiments and data collection needs to be done to generalise the correlation factor. The manipulation of sample volume could also have a significant effect, especially for the implementation in rapid detection application.

## C. Quantitative (Absorbance against concentration)

In this test, the relationship between absorbance and concentration was obtained by fixing the light source into monochromatic light. The light was set to 495 nm as determined and discussed previously. Two indicators used to measure the performance of the absorbance and concentration relationship are the linearity of calibration curve and the repeatability of the measurement.

### i. Linearity of calibration curve

Figure 3 shows the calibration curve obtained to represent the relationship between optical absorbance and $Mn^{2+}$ concentration. The absorbance increased as the concentration of manganese increased, which is in agreement with our initial hypothesis, i.e., as the colour of solution is getting darker (i.e., concentration increases), more light will be absorbed. For this range of concentration, the reading from the spectrometer gives absorbance values between 0.5 and 2 and the values vary proportionally to the concentration. These values correspond to the transmittance of the monochromatic light (495 nm) through the samples at different concentrations. From the plot, the linearity can be determined based on the value of $R^2$, which is found to be 0.9963. This value indicates a high correlation between these two parameters, thus indicating the suitability of optical absorbance in measuring $Mn^{2+}$ concentration at the range of interest.

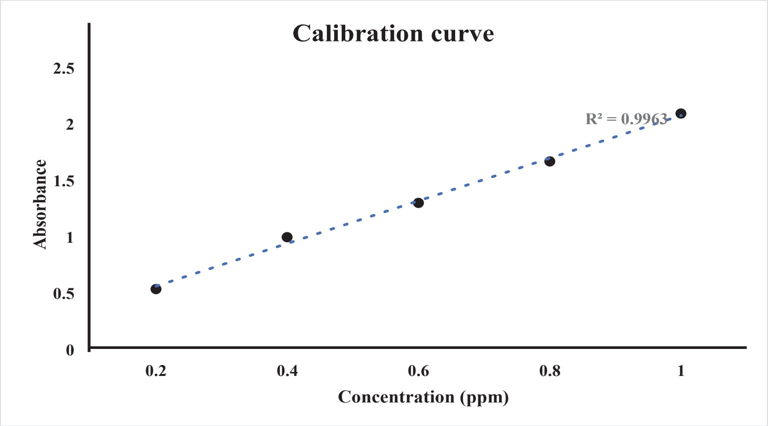

**Figure 3: Calibration curve (each point represents the average value of five different sets of colorimetric assay)**

As each point in the plot represents the average of five different sets of concentration samples, the consistency of data needs to be verified. For that reason, the $\sigma^2$ of each point concentrated sample was calculated and given in Table 3.

**Table 3: Standard deviation of five different samples of colorimetric assay**

| Concentration of Manganese (ppm) | Standard Deviation of Absorbance, $\sigma^2$ |
|---|---|
| 0.2 | 0.0293 |
| 0.4 | 0.0657 |
| 0.6 | 0.0625 |
| 0.8 | 0.0653 |
| 1.0 | 0.0420 |

It is found that the $\sigma^2$ for each point is very small, which means that the data points are close to the mean values. This indicates that the procedures used in preparing the samples and collecting the data give a good consistency of the measurements. This finding is important to ensure the reproducibility of the experiment, which is crucial in order to reduce the error that can lead to systematic error. Overall, these performance indicators verify the PAN method used in the sample solution preparation of colorimetric assay. Therefore, the method is considered to be suitable to be used in future work that requires such colorimetric assay to be prepared before the calibration curve can be obtained.

### ii. Repeatability of measurement

The reliability of the measuring instrument was measured through its repeatability test. Figure 4 shows the distribution data of three consecutive measurements taken for the final samples of colorimetric assay to observe any variation that could be due to instrumental error. Such error could originate from instrumental factors, such as calibration and drift issues, which could also lead to systematic error.

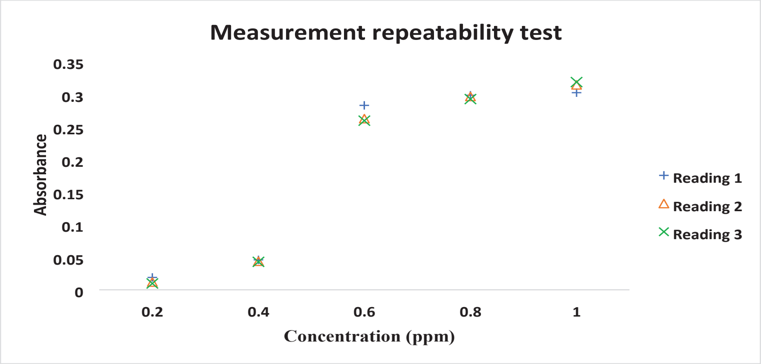

**Figure 4: Repeatability test (one set of colorimetric assay measured for three consecutive times)**

At a glance, it is observed that the absorbance data are well distributed for each concentration of the sample. The absorbance at two concentrations, i.e., 0.4 and 0.8 ppm, shows the best distribution, whereas at the concentrations of 0.6 and 1 ppm, the distributions are slightly scattered. The calculated $\sigma^2$ for all measurements gives a more precise indication of the scattering behaviour of the data. Table 4 shows the $\sigma^2$ of absorbance measurement for the repeatability test extracted from Figure 4. Throughout all concentrations, the deviations are found to be very small, ranging from 0.0015 (at 0.4 ppm) to 0.0125 (at 0.6 ppm). A small deviation error indicates that the use of the same measuring instrument is important in producing calibrated reference samples to be used for the comparison with the sample produced by the colorimeter to be proposed in the future.

**Table 4: Standard deviation of three repeated measurements for one set of colorimetric sample**

| Concentration of Manganese (ppm) | Standard Deviation of Absorbance, $\sigma^2$ |
|---|---|
| 0.2 | 0.0047 |
| 0.4 | 0.0015 |
| 0.6 | 0.0125 |
| 0.8 | 0.0031 |
| 1.0 | 0.0083 |

The result indicates a good repeatability of the spectrometric measurement used in this work, thus verifying the reliability of the instrument used in generating the calibration curve in this work. The curve is meant to be compared to the calibration curve that will be obtained in future development of monochromatic light-based colorimeter, provided that all procedures, settings, and precautions taken are maintained.

## CONCLUSION

As a conclusion, the main objective of this work has been successfully achieved. The spectroscopy method is successfully executed to identify several design requirements for future implementation in the colorimeter setup based on the use of a low-cost monochromatic light source, such as LED. The wavelength in the range of blue to cyan region is found to have the best option due to its maximum absorbance effect for monochromatic optical sensing implementation. Sufficient time interval is also identified as the parameter that allows complete colorimetric reaction to occur to ensure the measurement is taken at its stable state condition (i.e., at specific volume). Through calibration curve and repeatability test, the procedures and instrument used in sample preparation to find the relationship between absorbance and concentration are verified. These steps are important as the guidelines where the same technique is going to be replicated in our future work on low-cost colorimeter system development. The obtained calibration curve in this work can be compared with the calibration curve to be obtained in the future colorimeter system to validate the overall operation of the system.

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