On the determination of manganese in the presence of iron in pregnant leach solution using derivative spectrophotometry

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Abstract. Mn determination in samples with high Fe content using derivative spectrophotometric method was proposed in this paper, which formaldoxime was used as chromogenic reagent. The derivative method is useful to manipulate spectra data in order to eliminate the noise spectra i.e. Fe and isolate the spectra of elements of interest (Mn). Formaldoxime was chosen since the reagent reacted both to Mn and Fe at the same pH condition. In this paper, the accuracy in Mn determination in the presence of Fe using proposed method would be assessed and discussed. Mn and Fe could be simultaneously determined Mn using zero crossing point of first derivative Fe-formaldoximate spectra at 530 nm for Mn determination, while Fe could be predicted using zero crossing point of second derivative Mn-formaldoximate spectra at 469 nm. Maximum concentration which obeyed the linearity of calibration curve is 2 and 20 mg/L for Mn and Fe, respectively. The error in Mn and Fe prediction depends on ratio of both elements.

1. Introduction

The increasing needs for manganese to satisfy the demand in many industrial applications such as steel-alloy, chemicals and electronics [1] have sparks the interest for manganese resource exploration including its processing even for the low grade ones. To support these activities, reliable analysis method is mandatory. Several standard Mn determination methods in laboratory include atomic absorption spectrophotometry (AAS), induced couple plasma-atomic emission spectrometry (ICP-AES) and UV Vis spectrophotometry or photometry, which had been applied in all stages of mineral industry from prospecting phase until product quality control. The Mn content in sample is generally considered the key factor in choosing the method. In the case of Mn content falls in the range 0.1-100 ppm, UV Vis spectrophotometry is the best method due to its versatility and low capital cost.

Numerous protocols to determine Mn using UV Vis spectrophotometry had been proposed, which depended on special chemical reagent (chromogenic reagent) to develop the colour, including [2], [3], [4], [5]. Generally, these chromogenic reagents are not selective for Mn determination and reacts with other elements especially iron (Fe), which is omnipresent with high content compared to Mn. Hence, preliminary separation step such as ion exchange [3,5] and addition of masking agent to make other elements unreacted toward chromogenic reagents are required in the protocols.

To address the problem in Mn determination in samples with high Fe content, in this research derivative spectrophotometric method would be proposed, which formaldoxime was used as chromogenic reagent. The derivative spectrophotometry method is useful tools to manipulate spectra data in order to eliminate the noise spectra i.e. Fe and isolate the spectra of elements of interest (Mn). Formaldoxime was chosen since the reagent reacted both to Mn and Fe at the same pH condition. In
this paper, the accuracy in Mn determination in the presence of Fe using proposed method would be assessed and discussed.

2. Experimental
The chromogenic reagent, formaldoxime was prepared by mixing 7.9 ml formalin solution (38%) with 7 gr of hydroxylammonium hydrochloride (Merck, Darmstadt). The mixture was then diluted with deionized water to 100 ml in standard volumetric flask. Other chemicals such as potassium sodium tartrate, sodium hydroxide, Mn and Fe stock solution (1000 mg/L) for AAS were purchased from Merck, Darmstadt and used without further purification. Series of Mn and Fe standard solution to obtain calibration curve were made by mixing an aliquot of Mn or Fe stock solution with 0.5 ml of potassium sodium tartrate solution (20%), 1 ml formaldoxime solution, 0.25 sodium hydroxide solution (10 M) in standard volumetric flask and marked with deionized water. Binary mixtures of Mn and Fe with varied content and ratio, treated as samples were prepared as same manner.

The absorption spectra of Mn and Fe formaldoximate complex were collected using Perkin-Elmer Lambda 365 Spectrophotometer (USA), using 1 mm standard cuvette. Spectral bandwith and scan speed were 1 nm and 200 nm/min, respectively. Derivative spectra were generated using UV Express software, scan mode and smoothed using Savitsky-Golay algorithm for spectra smoothing.

3. Results and discussion

3.1. Mn direct determination
Mn in the form of MnO₂ in basic solution would react with formaldoxime to form brown colored complex Mn-formaldoximate. Other Mn species such as Mn²⁺ in basic solution was tended to be oxidized by oxygen in the solution to form MnO₂. Other species with higher oxidation state such as MnO₄⁻ would be reduced by formaldoxime to tetravalent Mn and then complexed by the formaldoxime [4]. Based the scanning result, the maximum absorption was attained at λ 450 nm (Figure 1). At this wavelength, Lambert-Beer law is obeyed for Mn content 0.1-2 mg/L (R² 0.9948) and molar absorptivity value ε 1.04 x 10⁴ L mol⁻¹ cm⁻¹.

![Figure 1. Mn-formoldoximate spectra (a) 0.91 mg/L and (b) 2.03 mg/L, Fe-formoldoximate-tartrate spectra (c) 2.55 mg/L and (d) 11.35 mg/L.](image)

3.2 Fe direct determination
The hydrolysis of trivalent iron (Fe$^{3+}$) in basic solution was hindered by the presence of tartrate, and reacted with formaldoxime to form purple colored complex. Spectra scanning of Fe-formaldoximate-tartrate is shown in Figure 1, with maximum absorption occurred at $\lambda$ 528 nm. At this wavelength, Lambert-Beer law is obeyed between 0.6 and 20 mg/L Fe, with molar absorptivity value $\varepsilon$ $2.02 \times 10^{3}$ L mol$^{-1}$ cm$^{-1}$.

3.3 Mn determination in the presence of Fe

As explained before, both Mn and Fe reacted with formaldoxime to form colored complex in basic condition. Derivative spectra of both complexes, reconstructed using UV Express software are shown in Figure 2. In the figure, at first derivative spectra, the derivative values of Fe-formaldoximate complex become zero regardless the Fe concentration at $\lambda$ 398 and 530 nm. These wavelengths are the zero crossing point of Fe spectra and at these wavelengths Mn could be determined. The linear calibration curve to determine Mn at 398 nm is $A = (2.666C + 0.123)x10^{-3}$ ($R^2$ 0.9985), and at 530 $A = (-1.061C - 0.016)x10^{-3}$ ($R^2$ 0.9994), where $A$ and $C$ are derivative value (y axis) and Mn concentration, mg/L (x axis) respectively.

![Figure 2](image)

**Figure 2.** First derivative of Mn-formaldoximate spectra (a) 0.91 mg/L and (b) 2.03 mg/L. Fe-formaldoximate-tartrate spectra (c) 2.55 mg/L and (d) 11.35 mg/L. Zero crossing points of Fe-formaldoximate-tartrate spectra are indicated by arrows.

To determine the Fe content in samples, second derivation of spectra is used, shown in Figure 3. In second derivative spectra, zero crossing point for Mn-formaldoximate complex occurred at $\lambda$ 469 nm. The linear calibration curve to determine Fe content using second derivative spectra at this wavelength is $A = (-0.0373C-0.0467)x10^{-4}$ ($R^2$ 0.9989), where $A$ and $C$ are derivative value (y axis) and Mn concentration, mg/L (x axis) respectively.

Table 1 shows the results of Mn and Fe determination using first derivative at $\lambda$ 398 and 530 nm (Mn) and second derivative at $\lambda$ 469 (Fe) including the error. Based on the error value in Table 1, the calibration curve using zero crossing point of Fe-formaldoximate at 530 nm of first derivative spectra is better in estimating Mn content than of 398 nm. At 530 nm, Mn in six out of seven samples could be predicted with error value less than 7%. Higher error tended to occur in samples with high Fe content. In the case of Fe, using zero crossing point of Mn-formaldoximate spectra at 469 nm, out of seven samples, six could be predicted with error less than 7%. The relation between error and Mn/Fe mass...
ratio in samples is demonstrated in Figure 4. In Mn prediction, first derivative at 530 nm had better correlation than of 398 nm, but both agreed that higher ratio of Mn/Fe would result in better prediction. In the case of Fe prediction using second derivative spectra at 469 nm the figure shows that higher error occurred for samples with high Mn/Fe ratio (Fe content was smaller than Mn). Based on the figure it could inferred that if the maximum error is set at 5, then the minimum ratio of Mn/Fe for Mn determination is 0.125 or maximum 0.14 for Fe determination.

| Added (mg/L) | Mn Found (mg/L) 1st, 398 | Error (%) | Mn Found (mg/L) 1st, 530 | Error (%) | Fe Found (mg/L) 2nd, 469 | Error (%) |
|--------------|--------------------------|-----------|--------------------------|-----------|--------------------------|-----------|
| Mn           | Fe                       |           |                          |           |                          |           |
| 1.11         | 0.96                     | 1.09      | -1.78                    | 1.11      | 0.93                     | -2.24     |
| 1.41         | 19.36                    | 1.26      | -10.75                   | 1.50      | 18.80                    | -2.93     |
| 1.04         | 14.79                    | 1.04      | -0.24                    | 1.15      | 13.80                    | -6.68     |
| 0.90         | 4.75                     | 1.12      | 24.42                    | 0.92      | 5.05                     | 6.21      |
| 1.99         | 19.04                    | 1.81      | -9.10                    | 2.08      | 19.45                    | 2.14      |
| 2.07         | 14.66                    | 2.01      | -2.92                    | 2.19      | 14.09                    | -3.83     |
| 1.99         | 11.38                    | 2.00      | 0.65                     | 2.02      | 14.28                    | 25.43     |

Table 1. Results of Mn and Fe determination in samples

Figure 3. Second derivative of Mn-formaldoximate spectra (a) 0.91 mg/L and (b) 2.03 mg/L. Fe-formaldoximate-tartrate spectra (c) 2.55 mg/L and (d) 11.35 mg/L. Zero crossing points of Mn-formaldoximate spectra are indicated by arrows
Figure 4. Correlation between Mn/Fe ratio and error (%) for Mn prediction using 1st derivative at 398 nm (a), at 530 nm (b), and Fe prediction using 2nd derivative, 469 nm (c)

4. Conclusions
Mn and Fe could be simultaneously determined using spectrophotometric method using formaldoxime as chromogenic reagent. Mn could be predicted using zero crossing point of first derivative Fe-formaldoximate spectra at 530 nm, while Fe could be predicted using zero crossing point of second derivative Mn-formaldoximate spectra at 469 nm. Maximum concentration which obeyed the linearity of calibration curve is 2 and 20 mg/L for Mn and Fe, respectively. The error in Mn and Fe prediction depends on ratio of both elements.

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