Square-wave voltammetric method for the determination of trace levels of manganese(II) and its application to the analysis of low alloy steel

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Received 3 September 2001; revised 1 November 2004

A highly sensitive, rapid and simple square-wave voltammetric procedure for the determination of Mn(II) has been developed. Mn(II) in triethanolamine (0.1 M) and KOH (0.15 M) gives a well-defined, reversible peak at -0.456 V vs. Ag/AgCl. The calibration curve is linear in the concentration range of 0-100 µg/ml. The minimum concentration that can be determined is found to be 40 ng/ml (s.d. = 4.2%). Effect of various ions, which commonly occur with Mn(II), has also been studied. The procedure has been applied for the determination of Mn(II) in low alloy steel samples.

IPC Code: Int.Cl. 7 G01N 27/00

A systematic investigation of the square-wave voltammetric method for trace analysis is being carried out in our laboratory[12]. The present note reports a sensitive, rapid and simple square-wave voltammetric procedure for the determination of manganese(II).

The standard reduction potential of Mn$^{2+} + 2e^{-} \rightarrow$ Mn is -1.55 V versus NHE. Various electroanalytical techniques like DPP$^{13}$, DPASV$^{6}$, cathodic stripping voltammetry$^{7,8}$, adsorptive voltammetry$^{9}$ and adsorptive stripping voltammetry$^{10}$ have been employed for the determination of Mn.

In the present study, we tried to mask the interference due to Cu(II), by using reagents like citrate but this procedure was found to be ineffective. It was then thought of determining Cu(II) by another independent method. The Cu(II) content in the sample being known, the difference then gave the Mn(II) content in the sample.

Experimental

A Metrohm PGSTAT20 potentiostat/galvanostat coupled with Metrohm VA 663 electrode assembly was used for recording the polarograms. A three-electrode assembly consisting of SMDE as the working electrode, Ag/AgCl as reference electrode, and glassy carbon as auxiliary electrode was used.

A stock solution of Mn(II) (1 mg/ml) was prepared by dissolving MnSO$_4$·H$_2$O (AR) in doubly distilled water. Further dilution was made to prepare a working standard that contained 100 µg/ml of Mn.

Stock solution of Cu(II) (1 mg/ml) was prepared by dissolving 0.393 gms of CuSO$_4$·5H$_2$O in 100 ml of doubly distilled water. Aliquot of this sample solution was further diluted 10 times so as to get a required standard of 100 µg/ml.

Stock solutions of supporting electrolytes, triethanolamine (TEA) (2 M), KOH (3 M), and KNO$_3$ (1 M) were prepared in doubly distilled water. All reagents used were of AR grade.

Experiments were performed in the laboratory where the temperature was maintained at 26±1°C. Maximum suppressor was not used.

Procedure

To 2.5 ml of triethanolamine (2 M), was added 2.5 ml of KOH (3 M) and the solution was made up to 50 ml in a standard flask with doubly distilled water. The solution was completely deaerated by passing N$_2$ stream through the solution for 15 mins. The voltammogram for this blank solution was recorded using square-wave as an analytical technique with a frequency of 100 Hz, step potential of 1 mV and pulse amplitude of 20 mV. The potential was scanned from -0.22V to -1.4V vs. Ag/AgCl.

The solution was then spiked with 20 µl Mn(II) (100 µg/ml) and deaerated by passing N$_2$ through the solution for 5 mins. A well-defined peak at -0.456 V vs Ag/AgCl was observed. The peak current increased proportionally with increase in the concentration of Mn(II). Typical square wave voltammograms are depicted in Fig. 1.

Analysis of synthetic samples

Synthetic samples containing varying amounts of Mn(II) and other elements like Fe(II & III), Ni(II), Mo(II), V(V), Cr(III & IV) and Cu(II), and having a composition similar (as given in the Table 1) to that of low alloy steel sample were prepared so as to study the validity of the method.

The samples were subjected to similar chemical processes as that of the real samples.
It was found that of these elements only Cu(II) interferes in the determination of Mn; in fact Cu(II) gives a peak at a potential same as that of Mn(II). The peak current obtained was the sum of the currents due to Cu(II) and Mn(II). Citrate was tried as a masking agent but was found to be ineffective. Cu(II), was, therefore, determined independently in KNO₃ (0.1 M) as a supporting electrolyte. The difference gave the Mn(II) content in the sample.

**Determination of Cu(II)**

5 ml of KNO₃ (1 M) was taken in a 50 ml standard flask and made up to the mark with doubly distilled water. The solution was completely deaerated by passing N₂ stream through the solution for 15 mins. The voltammogram for this blank solution was recorded.

The solution was then spiked with 1 ml of synthetic sample and deaerated for 5 mins. A voltammetric peak due to Cu(II), at 0.025V (+0.01V vs Ag/AgCl) was obtained; this peak current was recorded. The solution was then spiked with known amount of standard solution of Cu(II) (1 mg/ml) and the voltammogram was recorded after purging with N₂ for 5 mins. Typical square wave voltammograms are depicted in Fig. 2. The difference in the peak currents before and after the addition of standard solution of Cu(II) gave the current due to added amount of Cu(II) and from this, the Cu(II) content in the sample was calculated.

**Determination of Mn(II)**

To 2.5 ml of triethanolamine (2 M), 2.5 ml of KOH (3 M) was added and the solution was made up to 50 ml in a standard flask with doubly distilled water. The solution was completely deaerated by passing N₂ stream through the solution for 15 mins. The voltammogram for this blank solution was recorded.

The solution was then spiked with 100 µl of synthetic sample solution and the polarogram was recorded after purging with N₂ for 5 mins. The peak current corresponds to the total amount of Cu(II) and Mn(II) present in the sample.

The solution was then spiked with known amount of standard solution of Cu(II) (100 µg/ml) and the voltammogram was recorded. The difference in the current, before and after the addition of standard solution of Cu(II), was due to the added amount of copper(II) and from this, current per microgram of copper(II) was calculated. Since the copper(II) content in the sample was already known [Cu(II) alone was determined in 0.1 M, KNO₃], the current due to only Cu(II) in the sample was calculated. This current was then subtracted from the total current, which gave the current due to Mn(II) alone in the sample.

The solution was then spiked with known amount of standard solution of Mn(II), purged with N₂ for 5 mins and the voltammogram was recorded. From this, current per microgram of Mn(II) was calculated. Since the current due to only Mn(II) in the sample was known, the Mn(II) content in the sample was then calculated.
Determination of Mn in low alloy steel samples

Stock solution of low alloy steel sample was prepared by dissolving 0.5 g of sample in 5 ml of (1:1) H₂SO₄ by heating on a sand bath. The solution was evaporated to near dryness. The residue was taken up in doubly distilled water and the solution was made up to 50 ml in a standard flask. Similar procedure as that for synthetic samples was adopted for the analysis of low alloy steel samples.

Results and discussion

The calibration curve was found to be linear in the concentration range of 0-100 μg/ml. The lowest amount that could be quantified was 40 ng/ml (std. dev.=0.0422).

The regression line is given by \( i=0.05731x +0.01122 \) \((r=0.99961)\), where \( i \) is the current in μA and \( x \) is the concentration of Mn in μg/ml.

Effect of KOH concentration

Mn(II) in triethanolamine (0.1 M) and KOH (0.15 M) gave a well-defined polarographic peak at -0.456V vs Ag/AgCl. The peak was found to be dependent on concentration of KOH. It was found that at lower concentrations (6 mM) the peak was observed at -0.320V vs Ag/AgCl. The peak shifts to more negative potential with increase in KOH concentration. Also, the peak current increased slightly with increase in KOH concentration and the base line was found to be properly defined. This remains nearly constant after about 0.1 M of KOH and therefore the KOH concentration was optimised to 0.15 M in the final solution.

Effect of various ions

The effect of various ions like Fe(II), Fe(III), Cr(III), Cr(VI), V, Ni(II), Mo(II) and Cu(II) was studied. It was found that Ni(II) could be tolerated up to 100-fold excess, Cr(III), Cr(VI), Mo(II) and V up to 2-fold excess and Fe(II & III) up to even 500-fold excess. It was found that these only Cu(II) interferes. The peak due to Cu(II) was observed at the potential same as that of Mn(II) and this has also been reported in the literature.² Masking agent like citrate was tried but was found to be ineffective. It was therefore thought of determining Cu(II) by another independent method. The Cu(II) content being known, the amount of Mn(II) in the sample could be easily calculated.

Analysis of synthetic and low alloy steel samples

Mn(II) content in the synthetic and low alloy steel sample estimated, as described in the procedure gave good results. Results obtained from the analysis are given in Table 1.

Acknowledgement

The authors wish to acknowledge Head, Analytical Chemistry Division, for his keen interest, help and many fruitful discussions. Assistance and help rendered by Dr. R S Chitre and Shri R G Dalvi is gratefully acknowledged.

References

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