

Rapid Determination of Manganese by Differential Pulse and Alternating Current (1st harmonic) Polarography

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Manganese(II) in trace amounts has been determined by differential pulse polarography (DPP) and alternating current (1st harmonic) polarography (ACP) in 0.01 M LiCl and TEA + NaOH (0.1 M each) supporting electrolytes respectively. Manganese(II) gives well-defined, diffusion-controlled, reversible waves with E_p of -1.472 V and -0.452 V versus Ag/AgCl (saturated KCl). Linear calibration plots are obtained from 10 ppb to 10 ppm and from 50 ppb to 10 ppm in DPP and ACP respectively, the minimum determinable limits being 10 ppb and 50 ppb respectively. Effect of various metal ions, which commonly occur with Mn(II) has also been studied. The DPP in TEA (0.2 M) + NaOH (0.1 M) medium has been successfully used for the determination of Mn(II) in high speed steel, coal ash and pharmaceutical products.

Many techniques such as stripping voltammetry^{1,2}, a.c. polarography^{3,4} and dpp⁵⁻⁷ have been employed for the microdetermination of Mn(II). Presently we have used differential pulse polarography and a.c. (1st harmonic) polarography (ACP) for the determination of Mn(II) at ppb level.

A Metrohm-E-506 polarograph with attached cell assembly was used for recording the polarograms. Electrode assembly consisted of a dropping mercury electrode (d.m.e.) as an indicator electrode, Ag/AgCl (saturated KCl) as a reference electrode and Pt metal as an auxiliary electrode. All chemicals used were of AR grade. Stock solutions (0.5 M) of the supporting electrolyte were prepared in triply distilled water; working solutions (0.1, 0.05, 0.01 M) were prepared by suitable dilutions.

Stock solution of Mn(II) was prepared in triply distilled water using $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ (AR) and standardized. The working solution contained 150 μg of Mn(II)/25 μl . All usual precautions of trace analysis were observed.

Procedure employed in DPP of Mn(II)

Lithium chloride (2.5 ml, 0.1 M) was taken in the cell and to this was added the maxima suppressor triton-X-100 (1 ml, 0.001%). The volume was made up to 25 ml. To this, Mn(II) solution (25 μl) was added. The solution was completely deaerated by passing dry N_2 for 15 min and the polarogram recorded against the blank under the following conditions: scan range = -1.2 to -2.2 V; scan rate = 4 mV/s;

$t_{\text{drop}} = 0.8$; $\text{mm}/t_{\text{drop}} = 1.0$; and pulse modulation amplitude = 10 mV.

Procedure employed in ACP of Mn(II)

Triethanolamine (TEA) and aqueous NaOH (2.5 ml, 1 M each) were taken in the cell and polarogram recorded under the conditions mentioned in differential pulse polarography with a.c. frequency of 75 Hz and phase angle of 0° .

Differential pulse polarography (DPP)

A variety of supporting electrolytes (neutral, organic and inorganic salts) were employed for recording differential pulse polarograms. Following electrolytes were studied for this purpose: KCl (0.1 M to 0.01 M); NaOAc (0.1 M to 0.01 M); NH_4Cl (0.1 M to 0.01 M); KNO_3 (0.1 M to 0.01 M); trisodium citrate (0.2 M to 0.05 M); disodium tartrate (0.2 M to 0.05 M); Na-oxalate (0.1 M to 0.01 M); Na-succinate (0.1 M to 0.01 M); Na-salicylate (0.1 M to 0.01 M); LiCl (0.1 M to 0.01 M) and sodium dihydrogen phosphate (0.1 M to 0.01 M).

Amongst these, LiCl solution (0.01 M) was found to be most suitable as it gave smooth base line, symmetric, reversible, diffusion-controlled peaks with evenly rising steps, and higher current values and high reproducibility.

The presence of Triton-X-100 ($4 \times 10^{-5}\%$) was found to give improved base line and peak symmetry as compared to others and hence was used as the maximum suppressor.

Current-concentration relationship was found to be linear in three concentration ranges: 10 ppb to 100 ppb, 0.1 ppm to 1.0 ppm, and 1 ppm to 10 ppm. The minimum determinable limit was found to be 10 ppb.

Amongst the various ions studied for interference study Zn(II), Cd(II) and Cu(II) could be tolerated up to a ratio of 1:25, Pb(II) up to 1:20 while Co(II), Mo(VI) tolerated up to 1:10 and V(V) up to 1:5 only. Iron(III) and Cr(III) interfered seriously in the determination of Mn(II). However, interference due to Fe(III) and Cr(III) could be overcome by using 0.2 M TEA + 0.1 M NaOH as the supporting electrolyte in which Mn(II), Fe(III) and Cr(III) peaks were well separated with peak potentials corresponding to -0.476 V, -1.316 V and -0.998 V respectively. Linear calibration plots of Mn(II) in the range of 0.1 ppm to 10 ppm were also obtained in TEA + NaOH medium. The recording parameters for this particular supporting electrolyte were as follows: scan range -0.2 to -1.7 V; scan rate = 6 mV/s; $t_{\text{drop}} = 0.8$, $\text{mm}/t_{\text{drop}} = 1$; and pulse modulation amplitude = 40 mV.

Table 1—Determination of Mn(II) in High Speed Steel and Coal Ash Samples

Sample	[High speed steel contains 0.27 g% Mn(II)]			
	Wt of Mn(II) (g%)			
	DPP Method		ACP Method	
	A	B	A	B
High speed steel samples (BCS)*				
1	0.2717	0.2634	0.285	0.270
2	0.2751	0.2746	0.270	0.260
Coal ash samples (wt of Mn(II) mg/g coal ash)				
1 Ramkrishna Godavari Valley coal field (AP)†	0.160	0.156	0.158	0.154
2 Bhatadi coal field, Wardha (M S)‡	0.048	0.0487	0.049	0.050

(A) Calibration method; (B) standard addition method
* RMD:1.98%; † RMD:1.273%; and ‡ RMD:1.175%

The method developed using TEA + NaOH was further extended for the determination of Mn(II) in high speed steel, coal ash and pharmaceutical products.

Determination of Mn(II) in high speed steel by DPP

Steel sample (0.3 g) was treated with 25% H₂SO₄ (50 ml) and the solution warmed gently till hydrogen evolution ceased. The contents were cooled and H₂O₂ (100 ml) was added to oxidize any carbide residue. The solution was boiled to expel excess of H₂O₂, cooled and the volume made upto 100 ml with triply distilled water⁸. The polarograms were recorded in TEA + NaOH medium with 1 ml and 2 ml aliquots of sample solution. The amount of Mn(II) was computed from calibration plots and ascertained by standard addition method. The results are presented in the Table 1.

Determination of Mn(II) in coal ash by DPP

To a weighed quantity of coal ash were added 1:1 HCl (25 ml) + conc. HNO₃ (1 ml) and heated to dissolve ash and to expel acid. This procedure was repeated two-three times and finally the volume was made upto 25 ml with triply distilled water. The polarograms were recorded in TEA + NaOH supporting electrolyte with 1 ml to 2 ml aliquots of the sample solution. The concentration of Mn(II) was determined by referring to the calibration curve and ascertained by standard addition method. The results are given in Table 1.

Determination of Mn(II) in drugs by DPP

Cyltab, a vitamineral tablet (Dupher-Interfran Ltd) was analysed for Mn(II) content. Total 5 tablets were taken in a beaker. Hydrochloric acid (10 ml) and a few

drops of H₂SO₄ were added to these and volume was made upto 25 ml with triply distilled water. The contents were heated for 3-4 hr, cooled, filtered and the filtrate evaporated to dryness. The residue was dissolved in triply distilled water (25 ml). An aliquot (1 ml) from this was placed in the cell and the polarogram recorded in TEA + NaOH medium. The amounts of Mn(II)/tablet were found to be 0.3531 mg and 0.35 mg by calibration and standard addition method respectively (literature, 0.355 mg/tablet).

Alternating current (1st harmonic) polarography (ACP)

A variety of electrolytes (alkaline, neutral complexing agents and buffers) were tried as background electrolytes for Mn(II) analysis. The current response and peak symmetry were observed to be the best in TEA + NaOH with relatively lower current value. The supporting electrolytes studied were: KCl (0.5 M to 0.01 M); Na-succinate (0.1 M to 0.01 M); KNO₃ (0.1 M to 0.01 M); NH₄OH + NH₄ succinate (0.1 M each); NH₄OH (0.1 M) + citric acid (0.05 M); NH₄OH (0.1 M), tartaric acid (0.1 M); and TEA (0.1 M) + NaOH (0.1 M).

Calibration plots obtained for Mn(II) in TEA + NaOH medium were linear in the Mn(II) concentration range of 50 ppb to 10 ppm. The lowest determinable limit was 50 ppb with relative mean deviation of 1.13%.

Amongst the number of diverse ions studied for interference studies, Cu(II), Co(II), Ni(II), Pb(II) and Zn(II) could be tolerated upto the ratios 1:10, 1:5, 1:7, 1:3 and 1:7 ratios respectively while Cd(II), Fe(III) and Cr(III) could be tolerated upto a ratio 1:25 only. The results of determination of Mn(II) in high speed steel, and coal ash using a.c. polarography are presented in Table 1.

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