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Notes

Optimization of manganese determination by voltammetry in presence of chromium and nickel

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The optimum conditions for the determination of manganese at low concentrations have been developed employing differential pulse polarography. The limit of quantification of 1.04 µg mL^{-1} has been achieved. The possible interference of coexisting metal ions has been examined and ruled out. The method has been successfully applied for the analysis of manganese in industrial waste samples.

Keywords: Manganese, DPP, Chromium, Nickel, Industrial waste analysis

Manganese and its compounds have wide industrial applications such as in making of stainless steel and ceramics. Permanganates are employed as disinfectant, oxidising agent, in metal cleaning, in tanning, bleaching, and as preservative. MnO_2 is used as depolarizer in dry cell batteries[1]. Thus, it is appropriate to develop an analytical method of simple approach for the determination of manganese in industrial wastes.

Several methods such as spectrophotometry[2], atomic absorption spectroscopy (AAS)[3], fluorescence spectrometry[4] and induced couple plasma mass spectroscopy (ICP-MS)[5] are reported in determination of microgram level manganese. Manganese exists in different oxidation states from Mn (I) to Mn (VII), Mn (II) being the most stable form[6]. Thus procedure require preliminary treatment of sample (by preoxidation or reduction) to bring Mn to the proper form for measurement.

Voltammetric methods such as differential pulse polarography (DPP) and stripping voltammetry are more suitable in such determinations[7]. These can identify and determine various ionic forms of an element due to the certain selectivity of the redox potential. In stripping analysis intermetallic compound formation on the electrode surface causes significant interference. Therefore suitability of DPP is examined in present work. Buffle and coworkers[8] have reported the determination of manganese in fresh water, biological materials and coal ash by pulse polarography. Piech *et al.,*[9] have determined manganese by anodic stripping voltammetry using mercury film silver based electrode. Ghoenim[10] has described adsorptive cathodic stripping voltammetric estimation of manganese in water samples. Bank *et al.,*[11] have shown detection of manganese in marine sediments at a carbon paste electrode by stripping voltammetry. Linear sweep voltammetric determination of manganese at a glassy carbon electrode is given by Zhang and Di[12], Mercury film electrode[13], carbon film electrode[14] and nano electrodes[15] are also reported in determination of manganese.

Herein, study of electroreduction of manganese (II) at dropping mercury electrode (DME) shows the possibility of developing a convenient method for the determination of manganese at low concentrations. The limit of quantification of 1.04 µg mL^{-1} was achieved using DPP.

Experimental

Instrumentation

A polarographic analyzer (Model CL-362) in combination with a drop timer assembly from Elico Ltd., Hyderabad, India, was used for polarographic measurements. Current voltage curves were recorded by an Epson printer (Model LX-300 + II). The instrumental settings for DPP were as follows: a DME was used as working electrode; pulse amplitude-25 mV; drop time- 0.5 s; scan rate- 12 mV/s and charging current compensation- 20%. Saturated calomel electrode (SCE) and a platinum wire were used as reference and auxiliary electrodes, respectively.

A Perkin Elmer atomic absorption spectrophotometer (Model-AA 2380) with a wavelength range of 1900-9000 Å was also used for sample analysis. The instrument has Czerny turner grating monochromator, sequentia facility and adjustable sample aspiration flow control. Point focus burner optics permits high sensitivity analysis by passing a light beam of very small size through the flame.

Sample preparation

Industrial waste water samples were collected in clean polyethylene containers. These were filtered in order to separate any suspended particulate matter. 100 mL aliquot of the sample was treated with 1 mL of an oxidizing mixture of nitric acid and hydrochloric acid to remove biological and other materials.

Materials

Chemicals used were of reagent grade purity. All solutions were made in purified water obtained from Elix (Milli Q Advantage A 10) of Millipore, SAS, France. Stock solution of Mn (II) was prepared from manganese chloride (Batch no. 104272 of Thomas Baker).

All experiments were carried out in an air-conditioned laboratory where the temperature was maintained at 25±1 °C. Test solutions were deaerated by bubbling nitrogen for 20 min prior to voltammetric recordings. Nitrogen was purified by passing it through a vanadous chloride scrubbing solution[16].

Results and discussion

Preliminary electrochemical observations of manganese (II) on a DME indicated the suitability of 0.5 M potassium chloride among other supporting electrolytes studied viz, 0.1 M $CaCl_2$, 0.1 M KOH and 1 M NaOH. A well defined DC polarographic wave was obtained with a half wave potential of –1.52 V. The linearity between peak height and manganese concentration was in the range of 1.04 to 16 ppm as shown in Fig. 1. The characteristics of calibration curve were as follows: slope- 0.047, intercept- 0.009, coefficient of correlation (r)- 0.988 (shown in Fig. 2).

Limit of quantification

The minimum amount of manganese which could be determined under these experimental conditions was 1.04 $\mu g\ mL^{-1}$.

Interference

In view of wide applications of manganese in manufacturing of steel, the interference of other coexisting metals such as chromium, lead and nickel was monitored during DPP measurements. DP peak of these metals were found distinguishable from each other (Ep: Cu(II) –0.18V; Pb(II) –0.43V; Ni(II) –1.05V and Cr(VI) –1.5V Vs SCE, illustrating no interference. It has been illustrated in Fig. 3.

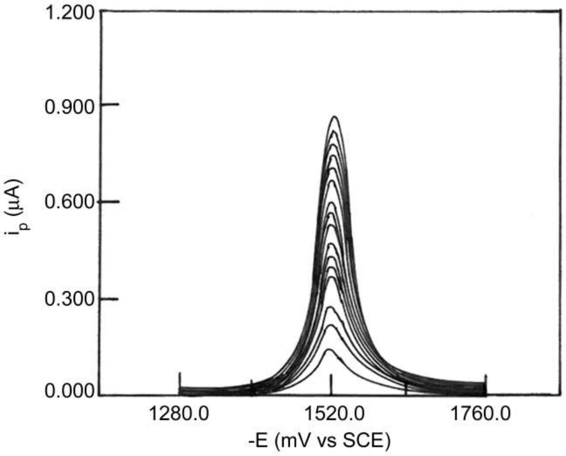

Fig. 1 — DP polarogram of manganese (II) at different concentrations.

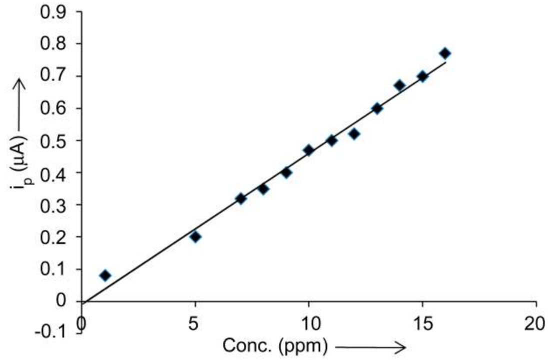

Fig. 2 — Calibration curve of manganese (II), concentration Vs peak current.

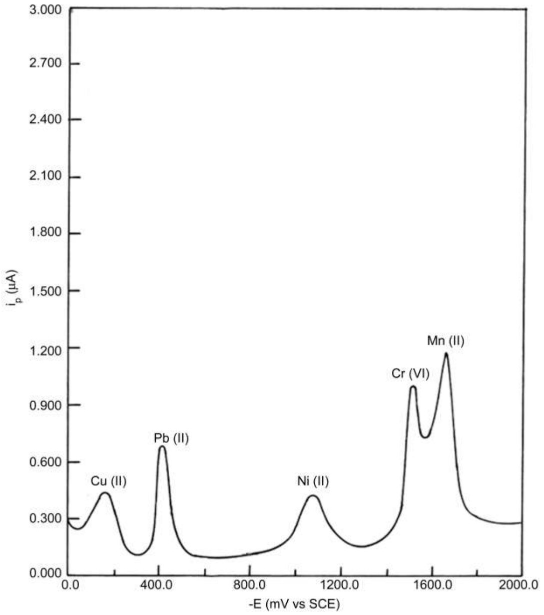

Fig. 3 — DP polarogram of Mn (II) in presence of copper, lead, nickel and chromium in 0.5 M KCl; Cu (II) 10 ppm; Pb (II) 10 ppm; Ni (II) 14 ppm and Cr (VI) 16 ppm.

Table 1 — Determination of manganese by DPP and AAS

Sample	Manganese (ppm)^n		
	DPP ± SD	RSD%	AAS
Mohnot Steels	1.30±0.026	2.0	1.33
Kansara Industries	4.86±0.096	1.97	4.79
Pushp creations	1.42±0.026	1.83	1.46
Common Nala#	1.20±0.043	3.58	1.23

# Located in Basni Area
n = No. of determinations, (n) = 4

Determination of manganese in industrial wastes

The prepared sample was taken into the polarographic cell with 0.5 M KCl and DP polarogram was recorded from 0.0 to –2.0 V. The peak current was measured at –1.5 V after making blank correction. The concentrations were determined by standard addition method[17].

The DPP results were further correlated with AAS method to compare the results obtained by both methods. The data are summarized in Table 1.

Conclusions

The proposed DPP method for the determination of manganese is more specific, sensitive and rapid. It has enabled trace determination of manganese in presence of chromium and nickel. The results of manganese determined by present method are also in good agreement with other techniques including DPP (concentration limit, 1×10^{-7} M to 2×10^{-6} M) in terms of measurement[18].

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