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Determination of Manganese by a Combination of Anodic Stripping Voltammetry and Differential Pulse Polarography

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Abstract

Manganese was preconcentrated on a hanging mercury drop electrode at -2.0 V vs. SCE and the concentrated manganese was stripped at -1.3 V. The stripped and concentrated manganese around the electrode was measured by differential pulse polarography. By this method, a considerably low level of manganese ($0.1 \mu\text{g/l}$) could be determined. Relative standard deviation was 10% at $2 \mu\text{g Mn/l}$ level. The method is interesting as a type of voltammetric analysis and can be applied to natural fresh water.

Introduction

Increasing attention has been given to chemical speciation of heavy metals in natural waters. Voltammetric techniques are increasingly used in studies of the speciation of heavy metals, because they are able to distinguish different chemical species. In heavy metals, iron and manganese are biologically important trace elements.

There have been a few reports of electrochemical measurement of manganese in natural waters. Davison^{1,2)} reported using polarographic methods in the analysis of manganese in lake waters in the concentration range of $0.1-5 \text{ mg/l}$. Knox and Turner³⁾ increased sensitivity ($10-300 \mu\text{g/l}$) for the determination of manganese by differential pulse polarography. Anodic stripping voltammetry (ASV) with a hanging mercury drop electrode has been reported⁴⁾ but the sensitivity is low ($50 \mu\text{g/l}$). Recently Ohalloran⁵⁾ increased the sensitivity (below $1 \mu\text{g Mn/l}$) by ASV by using a glassy carbon electrode coated with a mercury thin film. In his paper, he suggested that the application of ASV to environmental analysis and speciation studies of manganese will be addressed in a separate communication, and that the influence of pH and interferences from other co-deposited trace metals on the thin film electrode will be covered in detail. Since the ASV experiment was carried out in an alkaline solution, and its application to environmental analysis and speciation studies appeared to be difficult.

Experiment

Apparatus

A Yanaco P-1000 Voltammetric Analyzer was used with a hanging mercury

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drop electrode (Metrohm EA 290). A Watanabe X-Y recorder was used to record the polarographic data.

Procedure

Transfer 50 ml of a sample solution to an electrolysis cell, and add 0.4 g of potassium chloride. De-aerate with nitrogen gas for 10 min, stirring at 400 rpm. Preelectrolyze manganese at -2.0 V with stirring (400 rpm). Stop the stirring before 30 sec at the end of the timed preelectrolysis to prevent manganese on the electrode from being desorbed and turn off the applied potential. Allow to stand 1 min and turn back to -1.3 V by a hand within this period. Strip concentrated manganese at the potential of -1.3 V for 5 sec. Scan the electrode potential from -1.3 V to -1.7 V at a scan rate of 20 mV/sec with a 50 mV pulse amplitude.

Analytical conditions

Effects of stirring and standing times

The analytical conditions were studied for a solution containing $5 \mu\text{g Mn/l}$. The stirring and standing times before stripping are very sensitive to a reduction current peak of manganese because desorption of manganese on the electrode occurs. As shown in Fig. 1, 4 min of stirring are too long because concentrated manganese on the electrode is desorbed. The recommended stirring time is 4.5 min.

A standing time less than 40 sec is too short because a stripped manganese cloud around the electrode is disturbed. If the standing time is more than 80 sec, the reduction current peak of manganese decreases because stripped manganese around the electrode diffuses. As shown in Fig. 2, the best standing time is 60 sec.

Effect of stripping time at -1.3 V

A constant reduction current peak was obtained within 10 sec of the stripping time (Fig. 3).

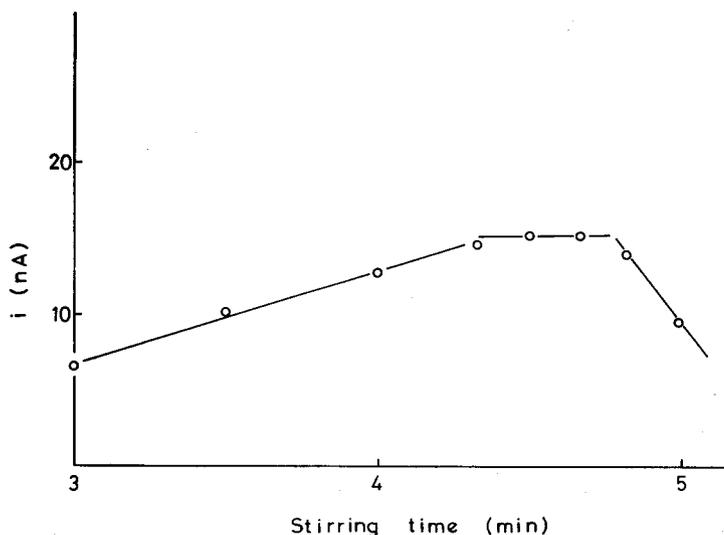


Fig. 1. Effect of stirring time

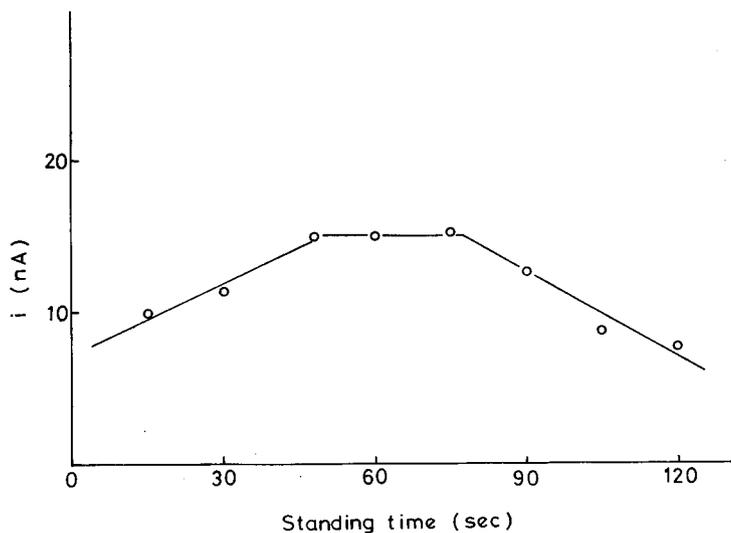


Fig. 2. Effect of standing time

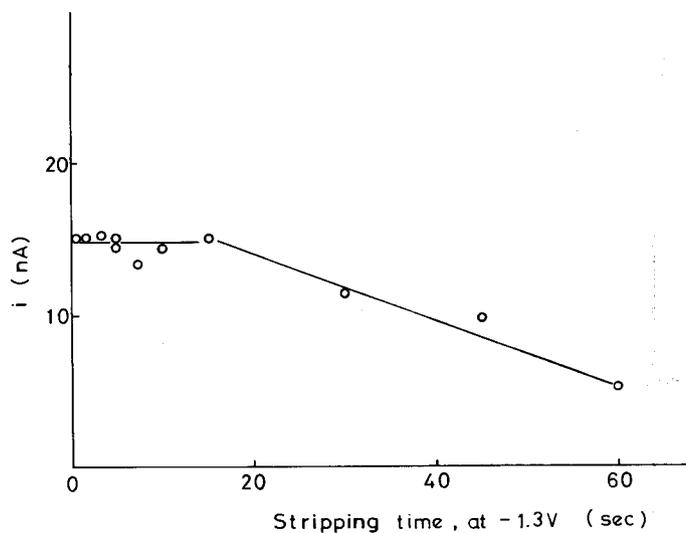


Fig. 3. Effect of stripping time

Effect of pH

As shown in Fig. 4, a constant reduction current peak was obtained in weak acid and weak alkaline solutions in the pH range from 5 to 8. Below pH 5, a hydrogen reduction wave disturbed the manganese reduction current peak, and especially, below pH 4, the reduction current peak of manganese was covered with the hydrogen reduction wave. Above pH 8, the manganese reduction current peak

decreased slightly. It is possible to increase the sensitivity by using a glassy carbon electrode coated with a mercury thin film, but in natural fresh water (pH 5–8) it is difficult to record manganese reduction current peaks because the hydrogen reduction wave shifts to positive potential and covers the manganese peak.

Voltammograms of manganese and their precision

The voltammograms of manganese in various concentrations are shown in Fig. 5. A working curve shows a straight line up to $20 \mu\text{g Mn/l}$. By increasing the preelectrolytic time, it is possible to determine manganese at a lower concentration.

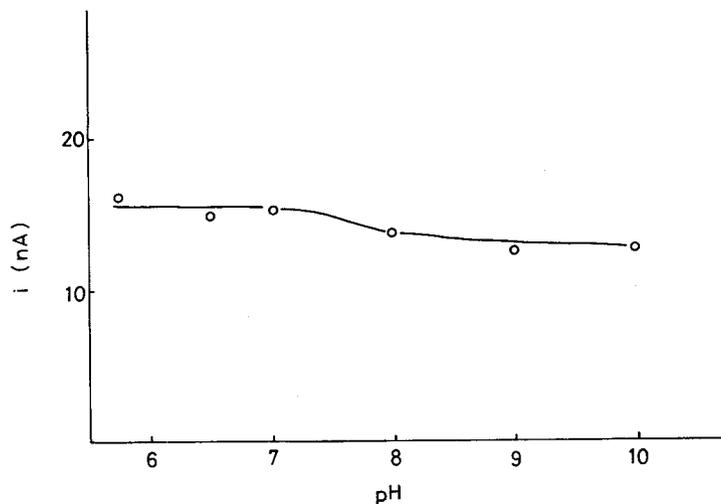


Fig. 4. Effect of pH

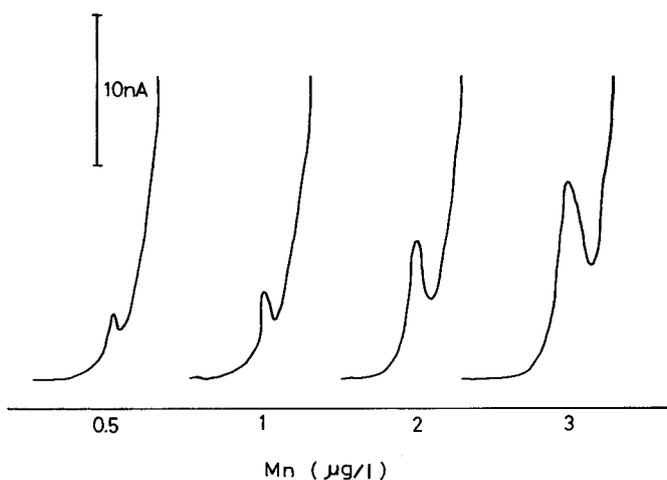


Fig. 5. Voltammograms of Mn in various concentrations

Table 1 *Manganese in fresh water samples*

Sample	Mn($\mu\text{g}/\text{l}$)
snow (1)	1.6
snow (2)	0.9
snow (3)	1.0
river (1)	0.3
river (2)	57*
river (3)	7.2

* Sample was diluted to 10 times with distilled water

The standard deviations of the procedure were determined by analyzing 2 μg Mn/l solution. The relative standard deviation for 5 replicate determinations was about 10%.

Determination of manganese in fresh waters

Manganese in river and snow samples was determined by the above procedure. The results are shown in Table 1.

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