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FLOW POLAROGRAPHY OF SODIUM(I) IN AIR-SATURATED SOLUTIONS

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Modified normal pulse polarography was applied to the determination of sodium(I) in flowing solutions. The interferences from dissolved oxygen and hydrogen ions were avoided by measuring the oxidation current of amalgamated sodium which is formed in pulse duration. This method is useful for the determination of metal ions in fluid streams.

Electrochemical detectors in liquid chromatography become popular for the determination of compounds such as catecholamines. But it is difficult to measure cathodic currents in amperometry without interference from dissolved oxygen, because dissolved oxygen in a mobile phase gives two cathodic waves in polarography and gives a large back ground current in amperometry. Therefore, polarographic methods, in general, necessitate the removal of dissolved oxygen from sample solutions. The continuous elimination of dissolved oxygen by a silicone tube is very interesting,[1,2] but increases the void volume. Furthermore, the dual working electrode method[3] and the reverse pulse amperometric method[4] make possible the monitoring of the effluents in the presence of oxygen. But they cannot distinguish even the components which have different half-wave potentials. In order to improve these defects, the polarographic determination of sodium(I) in air-saturated solutions was investigated by the use of modified normal pulse polarography (MNPP).[5-7]

The polarograph used was the one reported previously.[5] A simple flow cell was used, which has an L-shaped dropping mercury electrode(DME) shown in Fig. 1. The tip of the capillary was placed with a reference electrode and a counter electrode in a solution of supporting electrolyte in a 50 cm^3 beaker. The sample solution was continuously fed to the working electrode by a head of sample solution 10 to 40 cm high, and flowed out from the outlets placed above and below the tip of DME. The mercury drops of DME fall through the lower outlet. The flow rate of mercury, m, was 0.104 mg s^{-1}. The flow rate of the sample solution was adjusted by another glass capillary placed between the sample reservoir and the outlets. Tetramethylammonium sulfate was employed as a supporting electrolyte and was prepared by mixing a 10% aqueous solution

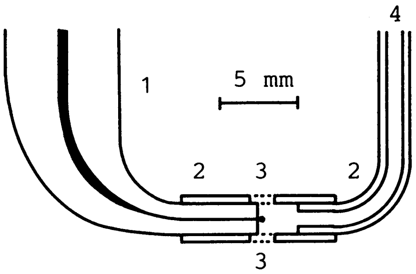

Fig. 1. L-shaped dropping mercury electrode for flow electrolysis.

1:glass capillary, 2:teflon tube, 3:outlet, 4:inlet.

of tetramethylammonium hydroxide and a dilute sulfuric acid.

The polarograms obtained by normal pulse polarography(NPP) and MNPP for the same air-saturated flowing solution are presented in Fig. 2. Curve 1 obtained by NPP has many waves, namely an anodic wave of mercury dissolution, reduction waves of oxygen, hydrogen peroxide, hydrogen ion, and sodium(I), respectively from left. It has a zero-current region in which neither the reduction of dissolved oxygen nor the oxidation of mercury of DME have occured. On the other hand, curve 2 obtained by MNPP has only a well-defined anodic wave of amalgamated sodium that was formed in pulse duration, and has no wave resulting from oxygen or hydrogen ions. In MNPP, a potential pulse whose width is T_2 is applied to DME after a delay time T_1 from the start of a new drop of DME, and current is measured after a short duration T_3 from the fall of each pulse. The pulse potential goes to the negative side pulse by pulse, and the potential of DME before and after the pulses is held at a constant value E_1. When E_1 of MNPP is set in the range of the zero-current potential of curve 1, the current after the pulse contains the oxidation currents of amalgamated sodium, hydrogen peroxide, and mercury. But the oxidation of hydrogen peroxide and the mercury dissolution by hydroxide ions at 0.1 V were negligible when the pH of solution adjusted by sulfuric acid is lower than 3.8. The relative standard deviation of the wave height for 4.33×10^{-4} mol dm^{-3} sodium(I) in an air-saturated solution of pH 2.5 was 0.33% for 5 runs.

As a very wide range of electrode potential is available in MNPP without the removal of dissolved oxygen, many kinds of metal ions in flowing solutions can be determined by this method. But some heavy metal ions require the addition of complexing agents to avoid the hydrolysis of the metal ions, because the concentration of hydroxide ions near the electrode surface is increased by the reduction of dissolved oxygen.

Furthermore, a three-dimensional detection in flow injection analysis and ion-exchange chromatography will be performed by a rapid scanning of the pulse potential of present method.

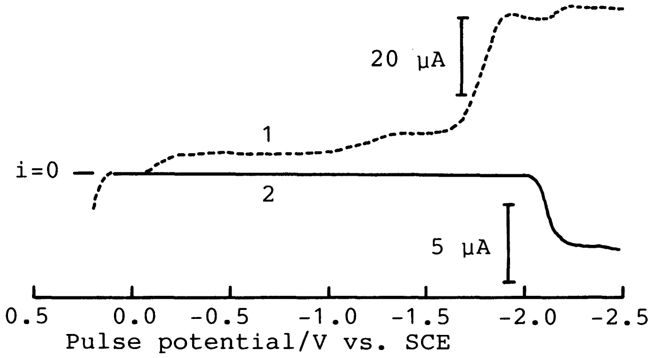

Fig. 2. Two types of pulse polarograms of sodium(I) in an air-saturated flowing solution.
Sample: 4.33×10^{-4} mol dm^{-3} Na(I) in 0.05 mol dm^{-3} $(Me_4N)_2SO_4$, pH=3.1. Flow rate:0.72 ml min^{-1}. DME: drop life=3.0 s, T_1=1.11 s, T_2=118 ms, T_3=2 ms, E_1=0.10 V.
Curve 1: NPP, curve 2: MNPP.

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