A.c. Polarographic Determination of Cyanide Ion after Conversion to Mercury(II) Cyanide by Use of Hg-form Resin

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Synopsis. Cyanide ion was converted to mercury(II) cyanide by shaking with Hg(II)-form resin and determined by a.c. polarography at pH 9.0. The recovery was 80.5%. A linear calibration curve was obtained in the cyanide concentrations ranging from 10^{-4} to 10^{-3} M (1 M=1 mol dm^{-3}).

As to the polarographic determination of cyanide ion, several methods have been reported,[1-4] which were mainly based on the anodic oxidation of mercury in the presence of cyanide. As early as 1937 the reduction of mercury(II) cyanide was studied in detail by Tomes.[5]

Experimental

Reagents. All chemicals used were of analytical reagent grade. A 10^{-2} M nickel(II) solution was prepared from sulfate and standardized against EDTA. A 10^{-2} M potassium cyanide solution was standardized against the nickel(II) solution. The solution of other metal ions was prepared from sulfate or nitrate and standardized against EDTA. A stock solution of mercury(II) cyanide was prepared by mixing the mercury(II) nitrate and potassium cyanide in the stoichiometric ratio. Buffer solutions used were 0.2 M boric acid —0.2 M sodium hydroxide (pH=8.0—11.0).

A cation exchanger Dowex 50 W-X8 (100—200 mesh) was washed as usual, converted into H-form and then air-dried. Five grams of the resin (2.79 meq/g) were treated with mercury (II) nitrate. The Hg-form resin was then washed with water and finally dispersed in water to give a suspension of 500-ml volume. The mixture was stirred each time before pipetting out.

Apparatus. The polarograph used was a Yanagimoto product, type P-8. Characteristics of the dropping mercury electrode were: m=1.88 mg s^{-1} and t=3.97 s in 0.5 M potassium nitrate solution containing the borate buffer in 0.02 M (pH=9.0) at an open circuit with a mercury column height of 72.5 cm. Polarograms were recoded at 25±0.1 °C. A Hitachi-Horiba glass electrode pH-meter, F-5 was used.

General Procedure. A 20-ml portion of smaple solution containing cyanide ion in the concentrations ranging from 10^{-4} to 10^{-3} M was taken into a separatory funnel and 5 ml of the Hg-form resin suspension was added. The mixture was shaken for 5 min at a room temperature. The resin was then separated by filtration through glass wool, and washed with about 10 ml of water. The filtrate and washings were transferred into a 50-ml volumetric flask containing 10 ml of 2.5 M potassium nitrate and 5 ml of the borate buffer (pH=9.0). The volume was adjusted to mark with water. A part of the solution was taken into a cell and oxygen was purged by passing nitrogen gas for 5 min. The dissolved oxygen interfered slightly when the concentration of mercury(II) cyanide is low. The a.c. polarograms were recorded succssively three times and the average peak current was measured.

Results and Discussion

Polarographic Behavior of Mercury(II) Cyanide. The direct current polarographic reduction of mercury-(II) cyanide has been studied by Tomes[5] and Newman *et al.*[6] In the pH range 6.0—9.5 was found a reversible wave corresponding to the over-all electrode reaction

$$Hg(CN)_2 + 2H^+ + 2e \longrightarrow Hg + 2HCN. \quad (1)$$

In alkaline solution $Hg(CN)_3^-$ and $Hg(CN)_4^{2-}$ are also reducible at the dropping mercury electrode.[6]

A well-defined a.c. polarogram with a stable and constant peak height was obtained in the pH range of 8.8 to 9.3, while the peak potential was shifted from —354 to —339 mV *vs.* Hg-pool. When mercury(II) ion is added in excess, however, precipitation of mercury(II) hydroxide takes place which causes the erroneous results. From the practical viewpoint, it is necessary to convert cyanide ion completely into mercury(II) cyanide without addition of excess mercury-(II) ion.

Use of Hg-form Resin. The mercury(II) cyanide being strongly stable,[7] it is expected that when cyanide ion is mixed with Hg-form resin mercury(II) ion is expelled form the resin into the solution forming mercury(II) cyanide as follows:

$$(RSO_3)_2Hg + 2KCN \longrightarrow 2RSO_3K + Hg(CN)_2, \quad (2)$$

where R denotes the resin matrix.

A 20-ml portion of sample solution containing 237 μg of cyanide was converted to mercury(II) cyanide and determined according to the above-stated general procedure. The procedure was repeated five times. The average peak current was 140 μS and relative

Table 1. Recovery of cyanide ion

Metal–cyano complex[a]	Temperature (°C)	Shaking time (min)	Conversion to $Hg(CN)_2$ (%)
KCN	room temp[b]	5	80.5
$K[Ag(CN)_2]$	room temp	5	81.1
$K_2[Ni(CN)_4]$	room temp	5	31.6
	room temp	60	81.0
	50	5	80.3
$K_2[Cd(CN)_4]$	room temp	5	80.3
$K[Cu(CN)_2]$	room temp	5	63.7
	50	5	67.9
$K_3[Co(CN)_6]$	room temp	5	4.5
	50	5	3.1
$K_4[Fe(CN)_6]$	room temp	5	28.3
	room temp	60	52.0
	50	5	37.5
$K_3[Fe(CN)_6]$	room temp	5	8.6
	room temp	60	81.1

a) Total cyanide ion concentration in the electrolysis solution was 4×10^{-4} M. Cyano complex was prepared by mixing the metal ion in small excess to the stoichiometric ratio. b) 17±2 °C.

standard deviation was 4.0%. On the other hand, the corresponding sample solution prepared from the stoichiometric mixture of cyanide and mercury(II) gave peak current of 174 μS ($n=3$). The conversion ratio was calculated to be 80.5%. The prolonged shaking time and the increased amount of resin have no effect on the improvement of recovery. The loss is not clearly explained, while the incomplete recovery is partly attributable to the formation of $Hg(CN)^+$.

A linear calibration curve of good proportionality was obtained in the cyanide ion concentrations ranging from 10^{-4} to 10^{-3} M. This means that the conversion ratio is constant in the above concentration range.

Silver(I) and cadmium(II) do not interfere with the formation of mercury(II) cyanide as shown in Table 1. In the presence of niekel(II) and iron(III) a prolonged shaking time or an elevated temperature is effective. Cobalt(III) combining with cyanide ion stronger than mercury(II) reduces the recovery seriously. Copper(II) and iron(II) also interfere.

When the concentration of chloride or thiocyanate exceeds twice that of cyanide, the recovery begins to decrease. An equimolar amount of sulfide interferes seriously.

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