A New Application of Neutron Activation Analysis to the Polarography of Holmium

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In general, two stepped reduction waves are observed in the polarograms of lanthanide elements. Conflicting explanations for the mechanism of electrode reaction have been reported as summarized in Table 1.

The present authors introduced a new method for the study of the electrode reduction process of holmium by utilizing a neutron activation technique. Assuming the electrode reaction of holmium to be $Ho^{3+}_{aq}+3e+Hg\rightarrow Ho(Hg)$, the amount of holmium $m(\mu g.)$ amalgamated in one drop of mercury is calculated by

$$m=i_1\cdot\tau\cdot 164.94/3F$$

where i_1 is the limiting current (microamp.), τ the drop time (sec.), 164.94 the atomic weight of holmium and F the Faraday constant. In the case of the experimental condition shown in Fig. 1, the amount of holmium that would be deposited is calculated as 0.022 μg. ($\tau=3.08$ sec.) for the first wave and 0.023 μg. ($\tau=2.67$ sec.) for the second wave. These amounts are well above the sensitivity limit of the activation analysis of the element[9].

One drop of mercury taken up immediately after electrode reaction* was sealed in a vinyl bag, and irradiated for two days with a neutron flux of $\sim 10^{11}$ $n/cm^2/sec.$ in the JRR-1 reactor. After irradiation, the induced radionuclide ^{166}Ho was purified by going through decontamination chemistry, and the amount of holmium was then determined by comparing the β activity of holmium from the sample with that of the monitor.

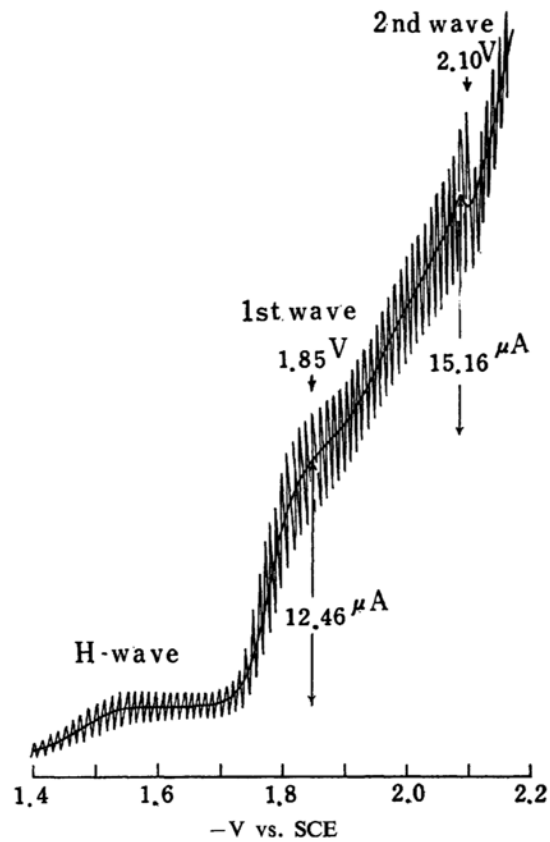

Fig. 1. Polarogram of 2.32×10^{-3} mol./l. Ho^{3+}. aq. in 0.1 N LiCl soln. containing 0.01% gelatine. Temp. 25.0±0.01 °C.
The 1st wave: Number of electron 3(pH< 3.1), temp. coeff. 3.0%, linear relationship between wave height and concentration is obtained. Reversible at pH<3.10, quasi-reversible at 3.10<pH<3.90, irreversible at pH>3.90 are explained by Matsuda-Ayabe's theory. $E_{1/2}$ shifts toward more negative with decreasing of pH.
The 2nd wave: Followed by a maximum wave, no linear relation between wave height and concentration is obtained, although the correlation between them is held. The ratio of wave height of the 2nd to that of the 1st is not 2 : 1.

Contrary to the earlier reports that had suggested a reduction of lanthanides to the metallic state, extremely smaller amount of holmium than was expected was found at both reduction steps as shown in Table II.

In the light of the above data and of the polarographic behavior shown in Fig. 1, it should reasonably be considered that the polarographic reduction of holmium is not the reduction of the holmium aquo-complex ion to a metallic state but the discharge of hydrogen ions

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* The method of collecting a drop of mercury is the same as that by J. J. Lingane and I. M. Kolthoff, *J. Am. Chem. Soc.*, **61**, 825 (1939).
In the present communication the re-dissolution of the deposited metal into the regulating solution, though possible, has not been taken into consideration.

TABLE 1. PROPOSED EXPLANATIONS FOR ELECTRODE REACTIONS OF LANTHANIDE ELEMENTS AT A DROPPING MERCURY ELECTRODE

Element studied	First wave	Second wave	Investigators
Sc, Y, La, etc.	$M^{3+}+e \rightarrow M^{2+}$	$M^{2+}+2e \rightarrow M^{0}$	Noddack, Bruckle[1,2]
Lanthanides except Eu, Yb	Hydrogen wave	$M^{3+}+3e \rightarrow M^{0}$	Kolthoff, Lingane[3]
La, Pr, Nd, Sm, Gd	$M^{3+}+3e \rightarrow M^{0}$	?	Glocker, et al.[4,5]
	$M^{3+}+e \rightarrow M^{2+}$ $M^{2+}+H_2O \rightarrow M^{3+}+OH^{-}+H^{0}$	$M^{2+}+2e \rightarrow M^{0}$	Purushottum, Raghava Rao[6]
Sm	$M(OH)^{2+}+3e \rightarrow M^{0}+OH^{-}$	?	Iwase[7]
Y	$M(OH_2)_6^{3+}+3e$ $\rightarrow M(OH)_3(OH_2)_3+3H^{0}$	?	Authors[8]

TABLE II. THE AMOUNT OF HOLMIUM (μg.) FOUND IN A DROP OF MERCURY*

First wave		Second wave	
m_{Ho}(found)	m_{Ho}(calcd.)	m_{Ho}(found)	m_{Ho}(calcd.)
0.0050	0.0218	0.0010	0.0230

* Values are corrected for the blank (0.0050 μg. Ho) in a drop of mercury.

produced by the dissociation of the aquo-complex ion. Details will be published later.

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