Determination of Microgram Quantities of Zirconium(IV) by a Catalytic Polarographic Method

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A simple polarographic method for the determination of microgram quantities of zirconium is developed based on the catalytic reduction of iodate by the metal ion. The catalytic wave consists of a peak at -1.4 V vs SCE. Interference of various anions and cations is investigated.

Many inorganic redox systems involving transition metal ions in higher valent state are known to catalyse the polarographic reduction of oxidants such as hydrogen peroxide, chlorate, perchlorate, nitrate, nitrite, bromate etc. These catalytic waves are exploited to develop senstive methods for the determination of metal ions present in trace quantities(1-3). Here is described a method of determining microgram quantities of zirconium in acetate buffer containing iodate. The results are communicated in this paper.

EXPERIMENTAL

All the chemicals used were of analytical quality. Zirconylchloride solution (0.1 M) and potassium iodate (0.1 M) are prepared in distilled water. Buffer solutions were prepared using sodium acetate and acetic acid.

A CL-25 Pen Recording DC Polarograph (Elico make) a ELICO Digital pH meter model LI-120 and a Lingane type of H-cell were employed to carry out these investigations.

RECOMMENDED

1 - 5 ml of zirconium(IV) of 1 x 10^{-4} M concentration, 6 ml of iodate of 0.1 M concentration and a required volume of distilled water are taken in a 25 ml volumetric flask. The solution is made upto the mark with a 0.2 M acetate - acetic acid buffer of pH 5.0, mixed well and transferred to the polarographic cell. Pure hydrogen gas is passed for about 15 minutes to remove dissolved oxygen. The polarogram is recorded.

A calibration curve is plotted with the data relating to the peak current and concentration.

RESULTS AND DISCUSSION

Typical polarograms of zirconium(IV) alone (A), iodate alone (B) and zirconium(IV) + iodate mixture(C) recorded in an acetate - acetic acid buffer solution of pH 5.0 are presented in Fig. 1.

An analysis of the figure reveals that zirconium does not produce any reduction wave under these experimental conditions. Iodate, on the other hand, exhibited a well defined wave with half-wave potential -0.6 V vs SCE. A mixture consisting of zirconium and iodate resulted in a wave with large peak currents at -1.4 V vs SCE. The effect of pH revealed that the polarographic wave showing the maximum has a well-defined shape and large current in solutions of pH 5.

The peak current varied linearly with the concentration of zirconium in the range 4-22 x 10^{-6}M and conc. of IO_3^- (12 - 26 x 10^{-3} M). The following facts, (a) the current peak is not suppressed by gelatin, (b) the peak current is larger than what is expected for a normal diffusion controlled reduction, and (c) the peak current is unaffected by the height of the mercury column confirm that the wave is of catalytic nature and may be due to the reduced Zr(0) species formed at the elctrode by the reduction of the zirconium(IV) species being reoxidized by iodate and electrochemically reduced at the electrode repeatedly. To assess the reproducibility of the results, replicate measurements were made. The standard deviation was calculated to be 0.0112 g/ml and the relative standard deviation 0.614%.

INTERFERENCE STUDIES

It was found that Cl^- , Br^- , I^- , CO_3^{2-} and ferricyanide do not interfere upto a 100-fold excess. Mo(VI), Cr(VI), Cr(III), Zn(II), Cd(II), Mn(II), Co(II), Ni(II), Fe(II) interfere when their respective concentrations exceed 10-fold concentration of zirconium. F^-, SO_4^{2-}, Fe(III), W(VI), V(V), thiocyanate, EDTA seriously interfere in the determination even when present in small concentrations.

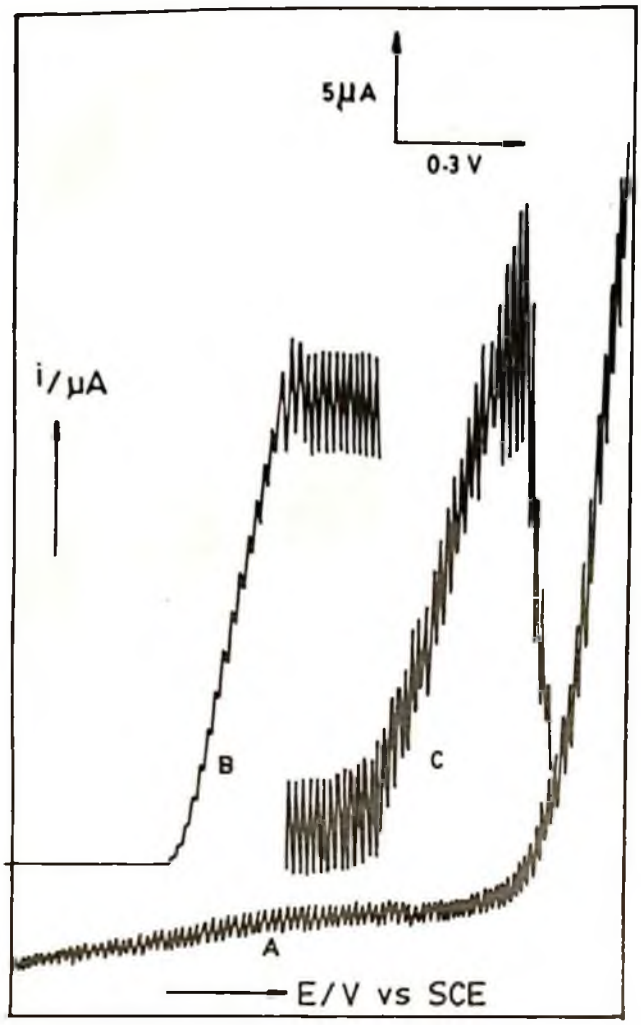


Fig. 1 Typical polarograms of

(A) Zirconium(IV) alone;
(B) Iodate alone and
(C) Zirconium(IV) + iodate mixture

[Zr(IV)] = 2×10^{-4} M
[IO_3^-] = 16×10^{-3} M
pH = 5

Starting voltages A = 0.6 V vs SCE
B = -0.3 V vs SCE
C = -0.9 V vs SCE.

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