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NOTES

Catalytic Polarographic Determination of Microgram Quantities of Zinc(II)

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A simple and sensitive polarographic method is developed for the determination of microgram quantities of zinc(II) based on the catalytic reduction of iodate. Salicylaldehyde thiosemicarbazone causes enhancement in current thus making the method more sensitive.

Many inorganic redox systems are known to exibit catalytic waves[1-6]. Polarographic catalytic waves are often used to develop sensitive methods for the determination of metal ions present in trace quantities[7-10]. During our investigations on catalytic waves involving iodate[11-13], it is noticed that Zn(II)-iodate system produces a reduction wave with a peak in ammonical medium (pH 9.0). Further, addition of salicylaldehyde thiosemicarbazone (SAT) to Zn(II)-iodate system enhances the peak current. The enhanced currents may be advantageously exploited to develop a sensitive method for the microgram determination of zinc(II) (1–50μ gms/ml). It may be pointed out here that no report is available in literature on catalytic reduction by zinc(II) ions.

Apparatus. A Cl-25 pen recording DC polarograph (Elico Pvt. Ltd., Hyderabad, India), a Lingane type H-cell and a Phillips model PP 9046 pH meter were employed. The voltages were measured against a saturated calomel electrode.

Reagents. All chemicals used were of analytical grade. Zinc sulphate solution (0.1 M) and potassium iodate solution (0.4 M) prepared in conductivity water with appropriate dilutions were used. Required amount of SAT is dissolved in 100 ml of DMF so as to obtain a 0.1 M solution. 2 M solutions of ammonia and ammonium chloride were employed to prepare the buffer solutions.

Calibration procedure. A 0.5–4.0 ml of 1×10^{-5} M zinc(II), 5 ml of 0.4 M iodate and 0.5 ml of 0.1 M SAT and required quantity of distilled water are taken in a 25 ml standard flask so that the total volume is always constant. The solution is made upto the mark with ammonical buffer of pH 9.0, mixed well and transferred into the polarographic cell. Pure nitrogen gas is passed for about ten minutes to remove the dissolved oxygen. Then the polarogram is recorded.

The peak currents corresponding to various concentrations of zinc(II) are determined, a graph is drawn between concentration of zinc(II) and peak current. A linear plot is obtained.

An analysis of the polarograms corresponding to individual chemical components and possible admixtures reveals that either zinc(II) or zinc(II) in presence of SAT does not show any reduction wave of appreciable size. This may be due to the low concentrations (10^{-6} M) of zinc(II) employed in these investigations. Polarograms recorded at a higher concentration of zinc(II) showed a wave at −1.05 V vs. SCE. Addition of SAT to zinc(II) causes a small shift in the wave (−1.10 V vs. SCE). The shift is due to the complex formation between the metal ion and thiosemicarbazone[14–15]. Iodate alone produces a wave at −0.63 V vs. SCE. On the other hand zinc + iodate mixture produced a peak and the potential corresponding to the peak is −0.7 V vs. SCE. Addition of salicylaldehyde thiosemicarbazone to the zinc-iodate mixture causes considerable increase in the peak current and this enhanced current can be utilised for the microgram determination of Zn(II) (1–50 μgs/ml). However, the peak potential is not influenced on the addition of SAT. The enhancement in peak current on the addition of complexing agents or hydroxy acids was reported by various workers[16–18]. They attribute the enhancement in current to the formation of surface active ternary complex involving the metal ion, oxidant and the complexing agent or hydroxy acid. The present authors also believe that a complex of zinc(II)-iodate and SAT formed at the surface of the DME is responsible for the enhanced current.

The height of the mercury column has no effect on the wave characteristics suggesting that the present wave is kinetic in nature; surfactants such as gelation, triton-X-100, agar-agar and methyl red do not cause any change in the wave characteristics. So also the observation of the mercury drop through a 'microscope' at the potential corresponding to the maximum revealed no streaming effects. Therefore the authors believe that the maximum is due to a chemical reaction.

It was found that even larger concentrations of Cl^-, Br^-, I^-, SO_4^{2-}, CO_3^{2-}, Cr(III), Fe(III) do not interfere in the determination of zinc, while Cd(II), Mo(VI), V(V), SCN^- interfere. Ni(II), Co(II), Mn(II) do not interefere upto a 10-fold excess.

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