Coulometric Argentometry of Microgram Amounts of Sulphide

Part I

Behaviour and Properties of Silver Sulphide-Silver Electrode in Ammoniacal-Alkaline Electrolytes

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Summary. The voltammetric behaviour of the silver sulphide-silver electrode in pure ammoniacal-alkaline electrolytes as well as in the presence of sulphide and the complex cation [Ag(NH₃)₂]⁺ have been investigated. It has been found that the silver sulphide-silver electrode behaves slightly irreversibly in ammoniacal-alkaline solutions of sulphide. On the basis of the results obtained the use of the silver sulphide-silver electrode for constant-current bipotentiometric and biamperometric end-point detection techniques appears to be convenient in the argentometric determination of sulphide.

Up to now only zero-current potentiometric end-point detection technique has been used in argentometric determinations of sulphide with silver sulphide-silver indicator electrode, and hence only the properties and
behaviour of this indicator electrode concerning the influence of different factors on its potential have been investigated. Thus Tamele, Irvine and Ryland studied the dependence of the potential of the silver sulphide-silver electrode on the concentration of hydrosulphide and silver ions. In the presence of silver ion the potential of the silver sulphide-silver electrode varied linearly with its concentration but in diluted solutions of hydrosulphide the shape of the potential-concentration dependence was irregular. The titration curves obtained were asymmetrical and the results received by means of a graphical treatment of the curves were therefore incorrect. Liu and Shen, who determined sulphide with silver sulphide-silver electrode in ammoniacal sodium hydroxide, also found the asymmetrical course of the titration curve at concentrations of sulphide below 10⁻⁴ m. The influence of silver sulphide precipitate on the potential of the electrode proved to be negligible during the course of the titration. On the basis of a good agreement between tabular and computed values of the solubility product of silver sulphide found out from the potentiometric measurements the silver sulphide-silver electrode was considered to be reversible in the given system. However, on the other hand, the silver sulphide-silver electrode was found to behave irreversibly in alkaline solutions of sulphide according to the measurements made by Golding in 1959.

In the present work some properties of the silver sulphide-silver electrode in ammoniacal-alkaline electrolytes found from the current-voltage curves are described. From the data obtained some further possible applications of the silver sulphide-silver electrode in determining sulphide by coulometric argentometry are pointed out.

**Experimental**

**Reagents and Solutions**. To follow the influence of sulphide a fresh standard solution of sulphide in 0.1 m sodium hydroxide containing approximately 0.2 mg of sulphide per ml was prepared. Hydrogen sulphide was produced by treating ferrous sulphide with hydrochloric acid in an apparatus thoroughly rinsed out with a stream of argon. 20 ml of the gaseous hydrogen sulphide were added by means of a syringe to the stream of argon passing through an absorber. The absorber was filled with 100 ml of 0.1 m sodium hydroxide, the dissolved oxygen of which had been stripped off by bubbling argon through it. The exact amount of sulphide in the standard solution was determined by iodometry. The standard solution of sulphide was kept under the argon atmosphere. Requested concentrations of sulphide in the electrolyte being investigated were prepared by delivering appropriate amounts of the standard solution of sulphide by means of an Agla syringe. Requested concentrations of silver were prepared by generating silver directly in the electrolyte being investigated.

All the reagents used were of the best reagent grade. Argon contained 20 ppm of oxygen.