Application Bulletin

Metrohm

Of interest for:
Photographic industry
General analytical laboratories

No. 72/1 e

Potentiometric determination of mercury or silver in the presence of halide ions

Summary

Halide ions interfere with most methods of determining mercury or silver. However, if mercury or silver are titrated with sulphide ions, extremely insoluble sulphides are produced.

A simple method is described which enables mercuric (Hg^{2+}) or silver (Ag^{+}) compounds to be titrated in the presence of halide ions. Potentiometric titration is carried out in an alkaline solution with thioacetamide as reagent, after forming an EDTA complex.

Organic compounds which are insoluble in alkaline EDTA can also be titrated after undergoing a Schöniger reaction.

Apparatus

- 2.536.0210 Potentiograph with 2.665.0030 Titrating stand or Titroprocessor
- 6.0404.100–Ag_2S Silver sulphide electrode (prepared by immersing an 6.0404.100 silver electrode in alkaline thioacetamide solution for 15 min)

Reactifs

- **pH = 5 buffer solution** Mix 0.1 mol/L potassium biphthalate solution with 0.05 mol/L trisodium phosphate in a proportion of 50:24. Dissolve 0.5 g thymol in 1 litre of this solution.
- **Thioacetamide 0.025 mol/L** Dissolve 1.9 g thioacetamide in 1 litre of the pH = 5 buffer solution. Standardise against silver nitrate. It has been found in practice that the titre of the solution remains fairly constant, diminishing by only about 1% per month.
  More dilute solutions are obtained by diluting with pH = 5 buffer solution.
- **NaOH 2 mol/L** Dissolve 80 g solid hydroxide in 1 litre distilled water.
- **EDTA 0.1 mol/L** Dissolve 37.2 g of the disodium salt of ethylene diamine tetraacetic acid in 1 litre distilled water.
- **Gelatine 1.2 %** Dissolve 12 g gelatine in hot water, add 0.5 g thymol, allow to cool and then make up to 1 litre.

Method

Pipette out 10 mL of the sample solution and allow it to react with 20 mL EDTA, 20 mL NaOH and 10 mL gelatine solution, and immediately titrate against thioacetamide solution of a suitable strength. The titration is carried out in the 100 mV range and runs from plus to minus. The alkaline solution should not be left standing too long before titrating, otherwise too low a result will be obtained.

1 mL 0.025 mol/L thioacetamide is equivalent to 5.015 mg Hg^{+2} or 5.394 mg Ag^{+}.

Remarks

- The gelatine solution prevents the agglomeration of the precipitates produced.
- In alkaline solution, thioacetamide forms sulphide ions. Owing to their solubility product with mercuric and silver ions (app. 10^{-50}), the halide ions are displaced out of the compound. This reaction is assisted by the formation of complexes with EDTA.

Literature

- Barbara Coulter/David G. Bush
  The titrimetric determination of mercury (II) with thioacetamide
  Anal. Chim. Acta 51, (1970), 431–436
- D.G. Bush/C.W. Zuehlke/A.E. Ballard
  Volumetric determination of silver using thioacetamide
  Anal. Chem. 31, (1959), 1368–1371