Acetylpyridine Thiosemicarbazone, an Analytical Reagent for Gold(III)

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2-Acetylpyridine thiosemicarbazone (APT) has been used as a spectrophotometric reagent for the determination of gold. Gold(III) forms a golden yellow coloured complex (1:3, metal-ligand) at pH 11 which exhibits maximum absorption at 460 nm ($\varepsilon = 1.5 \times 10^4$ litre mol^{-1} cm^{-1}). The method is sensitive and gives comparable results.

Numerous reagents are available for the extractive spectrophotometric determination of traces of gold[1-3]. Thiosemicarbazones are useful reagents for the spectrophotometric determination of transition elements[4]. In the present note, we have used 2-acetylpyridine thiosemicarbazone (APT) as a spectrophotometric reagent for the determination of gold.

Reagents and chemicals used were of AR grade. The reagent, 2-APT was synthesised from 2-acetylpyridine by the method of Pino[5] and recrystallised from ethanol, m.p. 158°. Its standard solution (5.1×10^{-3} M) was prepared in methanol. Solution of gold was prepared as follows: pure gold (100 mg) was dissolved in a few ml of aquaregia, solution evaporated to dryness on a water-bath, conc. hydrochloric acid (1 ml) added, the solution again evaporated almost to dryness, the residue dissolved in dil. hydrochloric acid and diluted to 100 ml with distilled water. Ammonia-ammonium acetate buffer was used to maintain pH 8-12.

The reagent solution in methanol exhibited maximum absorption at 340 nm in alkaline medium. The protonation constant pK_1 of the reagent was calculated from the values of $\bar{n}_H$ and K_1^H obtained by the usual Irving-Rossotti titrations[6,7]. The protonation constant was subjected to refinement using the computer programme SCOGS[8]. The refined value of 4.3 agreed with that obtained from the graphical method.

Determination of gold(III)

To an aliquot of gold solution containing 100 μg of gold(III) was added the reagent solution (2 ml), pH was adjusted to 11 and the solution diluted to 25 ml with buffer. The absorbance was measured at 460 nm after 45 min against reagent blank.

Au(III)—APT complex exhibits maximum absorption at 460 nm ($\varepsilon = 1.5 \times 10^4$ litre mol^{-1} cm^{-1}). The absorption due to the reagent at this wavelength is negligible. The complex can be partially extracted into chloroform. The complex formation occurs only in alkaline medium and full colour is developed after 45 min and the absorbance is constant and maximum in the pH range 10.5 to 11.5. The complex is stable over 24 hr at room temperature and at 40-60°C. It is also found that 0.75 ml of 5.1×10^{-3} M reagent solution is sufficient for gold solution containing 100 μg gold for complete complex formation. Beer's law is obeyed upto 10 ppm of Au(III) and the Ringbom's plot[9] indicates the optimum concentration range to be 4 to 9 ppm of gold. The composition of the Au-APT complex, as determined by Job's method of continuous variation and mol ratio method is 1:3 (metal-ligand). The Sandell's sensitivity is found to be 0.0156 μg/cm^2.

The degree of dissociation is calculated[10] to be 0.059 and the instability constant of the complex is 4.7×10^{-17}. The method is reproducible, precise and accurate.

Commonly associated ions like palladium, copper, ruthenium, rhodium do not interfere in the determination of gold when present in 50-fold excess, but silver and iridium interfere. Calcium, magnesium, beryllium, vanadium, iron, cobalt which are less commonly associated with gold do not interfere even when present in 100-fold excess. Synthetic mixtures of gold-palladium, gold-vanadium, gold-copper have been analysed and the results are found to be reproducible within 1.0%.

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