NOTES

SPECTROPHOTOMETRIC DETERMINATION OF TIN(IV) WITH PHENYLFLUORONE AND DODECYLTRIMETHYLLAMMONIUM BROMIDE

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The sensitizing effect of dodecyltrimethylammonium bromide (DTMAB) on the spectrophotometric determination of tin(IV) with phenylfluorone was studied. Under the optimum conditions the sensitivity was about twice as high as that without DTMAB. The calibration curve was linear up to 0.20 ppm of tin(IV). Polyvinyl alcohol (PVA), a commonly used dispersant, was not necessary. Metal ions such as Fe³⁺, Fe²⁺, Si, As⁵⁺, As³⁺, Pb²⁺, Cu²⁺, Sb³⁺, and Bi³⁺ did not interfere with the determination, while Ge⁴⁺ gave a positive error.

INTRODUCTION

Various spectrophotometric methods for the determination of tin(IV) have been proposed1)-8). The one with phenylfluorone2)-5) is most sensitive, and is adopted in JIS K 0101. Yamazaki et al9) reported that the addition of a quaternary ammonium salt, cetylpyridinium chloride increases the sensitivity of this method. The authors10) found that the addition of another quaternary ammonium salt, DTMAB increases the sensitivity and reduces the time required for development in the determination of germanium with phenylfluorone.

This paper deals with its application to the determination of tin(IV) with phenylfluorone, where the addition of DTMAB resulted in the increase of sensitivity and the reduction of the time required for full color development.

EXPERIMENTAL

Reagents

Standard tin solution (2 µg of tin per ml): Transfer 0.2000 g of pure tin metal (99.999%, Soekawa Rikagaku Co., Ltd.) into a 100 ml beaker, add 10 ml of sulfuric acid, and heat to dissolve the metal completely. Cool to room temperature, transfer to a 1000 ml volumetric flask, dilute to the mark with hydrochloric acid (1+4), and mix. Transfer 10 ml of this solution to a 1000 ml volumetric flask, dilute to the mark with hydrochloric acid (1+10), and mix.

Phenylfluorone solution (0.01 w/v%): Transfer 0.0500 g of phenylfluorone (Wako Junyaku Co., Ltd.) into a 200 ml beaker. Add 100 ml of ethanol and 10 ml of hydrochloric acid (1+2). Stir until complete dissolution. Transfer to a 500 ml volumetric flask, dilute to the mark with ethanol, and mix.
Hydrochloric acid-citric acid solution: Dissolve 10 g of citric acid (Kanto Kagaku Co., Ltd.) in a small volume of water to which 30 ml of hydrochloric acid has been added. Transfer to a 100 ml volumetric flask, dilute to the mark with water, and mix.

DTMAB solution (2 w/v %): Dissolve 10 g of DTMAB (Tokyo Kasei Co., Ltd.) in 500 ml of water.

All other reagents were of analytical reagent grade.

Apparatus

A Hitachi Model 228 double beam spectrophotometer with 1.0 cm silica cells was used.

Procedure

Standard procedure was chosen as follows on the basis of JIS method. Transfer 5 ml of standard tin solution (2 µg of tin per ml) into a 50 ml volumetric flask. Add potassium permanganate solution (1 w/v %) until the solution has turned slightly red. Stand for several minutes to allow tin to be oxidized. Add about 0.1 g of ascorbic acid and mix to reduce the excess potassium permanganate. Add 5 ml of hydrochloric acid-citric acid solution, then a certain volume of ammonia water (1+1) (enough to neutralize the standard tin solution), and then 5 ml of PVA solution (0.5 w/v %). Add 10 ml of DTMAB solution, 5 ml of phenylfluorone solution, and dilute to the mark with water. Swirl after each addition. Stand for 20 min. Transfer a portion of this solution to a 1.0 cm cell and measure the absorbance at 510 nm against a reagent blank.

Vary the concentrations of hydrochloric acid-citric acid, PVA, DTMAB, and phenylfluorone to find the optimal conditions for the maximum absorbance.

Absorption spectra

Spectrophotometric determination was carried out under the conditions mentioned above, where the maximum absorbance of the complex was obtained at 508 nm. It was nearly the same as for the case without DTMAB. This wavelength was employed for further measurements.

Effect of PVA concentration

The amount of PVA solution (0.5 w/v %) was varied in the range from 0 to 10 ml. A constant absorbance was obtained between 0 and 5 ml. It was found that the addition of PVA solution, which was indispensable as a dis-
persant in the conventional method, could be omitted because DTMAB also has a stabilizing effect.

Effect of DTMAB concentration
The amount of DTMAB solution (2 w/v%) was varied in the range from 1 to 20 ml. The result is shown in Fig. 1. A constant absorbance was obtained between 8 and 12 ml. Addition of 1 ml made the solution turbid after 30 min.

Effect of hydrochloric acid-citric acid concentration
The amount of hydrochloric acid-citric acid solution was varied in the range from 1 to 10 ml. The result is shown in Fig. 2. The absorbance decreased with the increase of reagent concentration. Addition of 1 ml made the solution turbid after 10 min.

Effect of phenylfluorone concentration
The amount of phenylfluorone solution (0.01 w/v%) was varied in the range from 3 to 15 ml. The result is shown in Fig. 3. A constant absorbance was obtained between 5 and 8 ml.

Recommended procedure
The following procedure was established from the above results. Put a series of aliquots of standard tin solution in 50 ml volumetric flasks and add a few drops of potassium permanganate solution (1 w/v%) until the solutions have turned slightly red. Stand for several minutes to allow tin to be oxidized. Add about 0.1 g of ascorbic acid and mix to reduce the excess potassium permanganate. Add 3 ml of

![Fig. 2 Effect of hydrochloric acid-citric acid solution concentration on absorbance](image1)

![Fig. 3 Effect of phenylfluorone concentration on absorbance](image2)
hydrochloric acid–citric acid solution, then a certain volume of ammonia water (1+1) (enough to neutralize each aliquot of the standard tin solution) and 10 ml of DTMAB solution. Add 5 ml of phenylfluorone solution, and then dilute to the mark with water. Swirl after each addition. Measure the absorbance at 508 nm against the reagent blank. Spectrophotometric determination was carried out with solutions containing 1 to 40 µg of tin. A linear calibration curve was obtained over the concentration range of 1 to 10 µg of tin. The molar absorptivity was $1.43 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$. Maximum absorbance was attained within a few minutes and remained constant for 2 h. When a series of fifteen standard solutions containing 10 µg of tin(IV) was analyzed, the relative standard deviation was 0.97%.

Effect of foreign ions

Effect of 10 foreign ions was investigated with the solution containing 10 µg of tin. No interference was given by a 1000-fold amount (in weight) of Fe$^{3+}$, a 500-fold amount of Fe$^{2+}$, a 100-fold amount of Si, As$^{5+}$, or As$^{3+}$, a 50-fold amount of Pb$^{2+}$, a 20-fold amount of Cu$^{2+}$, and a 10-fold amount of Sb$^{3+}$ or Bi$^{3+}$, while 1 µg of Ge$^{4+}$ gave a positive error of 15%.

CONCLUSION

A sensitive spectrophotometric method for determining tin(IV) with phenylfluorone was established by the addition of DTMAB. Beer's law is obeyed over the range of 0.02 to 0.2 µg of tin per ml, the molar absorptivity being $1.43 \times 10^5$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at 508 nm. Sensitivity was about 2 times as high as that without DTMAB, when the molar absorptivity was $7.12 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$. Maximum absorbance was attained within a few minutes and the addition of PVA solution was unnecessary, which led to the reduction of the time required for the determination.

REFERENCES


Keyword phrases
determination of tin(IV); spectrophotometry; quaternary ammonium salt; dodecyltrimethylammonium bromide; phenylfluorone.

(Received January 6, 1984)