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**SPECTROPHOTOMETRIC DETERMINATION
OF SILVER WITH BRILLIANT GREEN
AND ITS APPLICATION
IN PHOTOGRAPHIC FIXING SOLUTIONS**

**SPEKTROFOTOMETRYCZNE OZNACZANIE SREBRA
ZA POMOCĄ ZIELENI MALACHITOWEJ
W UTRWALACZACH FOTOGRAFICZNYCH**

Abstract: A simple spectrophotometric determination of silver in aqueous solutions was developed based on the reaction between AgI_2^- and Brilliant Green. This reaction results in, under appropriate conditions, an ion-associated complex which absorbs at $\lambda = 680$ nm and no extraction of this complex is needed. Silver ions could be determined satisfactory in the linear range $y = 0.00025x + 0.0432$ with $r^2 = 0.9973$ of 10–800 $\mu\text{g Ag}^+/\text{L}$. The interfering in the determination ions was examined. The proposed method proved to be successful in determining silver in photographic fixing solutions, that are many times disposed off in the environment, and the relative error of this method was found to be 4 %.

Keywords: silver, Brilliant Green, spectrophotometric determination, photographic solution

Over the last years several researchers have reported spectrophotometric determinations of silver by reactions between organic reagents and silver, such as Pal and Maity [1] with silver-gelatin interaction, Tarin et al. [2] with 4-(*p*-nitrophenylazo)-2-amino-3-pyridinol, Pilipenco et al [3] with Michlers thioacetone in the presence of anionic surfactants, Oshita et al [4] with 4-(3,5-dibromo-2-pyridylazo)-*N,N*-diethylaniline in the presence of sodium dodecylsulfate, Zhou Nant et al [5] with 5-[*p*-(dimethyl-amino)benzylidene]rhodanine] and Sanchez et al [6] with dithizone.

The objectives of our work was to develop a spectrophotometric method for Ag^+ determination, based on the formation of an ion association complex with Ag^+ and

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Brilliant Green in the presence of potassium iodide and to propose this method for silver determination in photographic fixing solutions.

Experimental

Apparatus

A Perkin Elmer, model Lambda 2 spectrophotometer was used for absorbance measurements. A Metrohm, model 503 pH meter was used for pH measurements.

Reagents

A BDH stock solution of $1000 \text{ mg/dm}^3 \text{ Ag}^+$ was used for the preparation of the working standards by proper dilution. An one g/dm^3 of Brilliant Green (MERCK) was prepared by dissolving in distilled water. Potassium iodide was used for preparing a solution of 5000 mg/dm^3 iodide ions. Sulfuric acid (0.025 and 0.50 M) and sodium hydroxide (0.1 M) solutions were used for pH adjustments.

Calibration

Suitable aliquots of the 10 mg/dm^3 standard silver solution or of the samples are placed in 50 cm^3 volumetric flasks. Silver concentrations must lie in the range of $10\text{--}800 \text{ }\mu\text{g/dm}^3$. One cm^3 of potassium iodide solution (5 g/dm^3) is added followed by aliquots of dilute H_2SO_4 or NaOH solution to bring the pH of the final volume to 3.0. Then, 0.75 cm^3 of the Brilliant Green solution (1 g/dm^3) are added. The flasks are immediately swirled, brought to volume with distilled water stoppered and shaken well. No extraction is needed. Measurements are taken at 680 nm 60 min after mixing the reagents.

Results and discussion

A large excess of iodide ions in a silver solution, is known to lead to the formation of the anion complex AgI_2^- . This anion reacts with Brilliant Green cation, giving an ion association complex of the type RAgI_2 (where R: the Brilliant Green cation).

The complex was practically formed immediately after mixing the reagents but the maximum absorbance value, which was found by measurements taken every 10 min, was obtained and stabilized after 60 min, and remained stable for at least 24 hours. The variation of the maximum absorbance value from the initial one, obtained 5 min after the mixing of the reagents was found to be about 25 % (Fig. 1).

The optimum experimental variables for the complex formation (regarding pH value and concentrations of KI and Brilliant Green) were estimated in a previous work [7], which concerned silver fluorimetric determination by formation of the same complex.

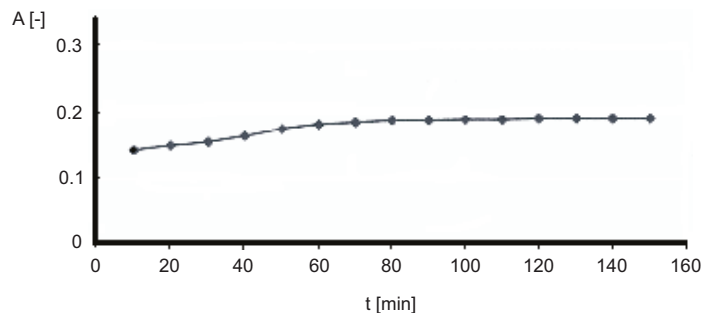


Fig. 1. Effect of time on the absorbance value

These are: pH = 3.0, concentration of KI = 100 mg/dm³ and concentration of Brilliant Green = 15 mg/dm³.

The measurements were taken at $\lambda = 680$ nm, because at this wavelength the repeatability of the measurements was better than the respective ones at $\lambda = 330$ and 460 nm (Fig. 2).

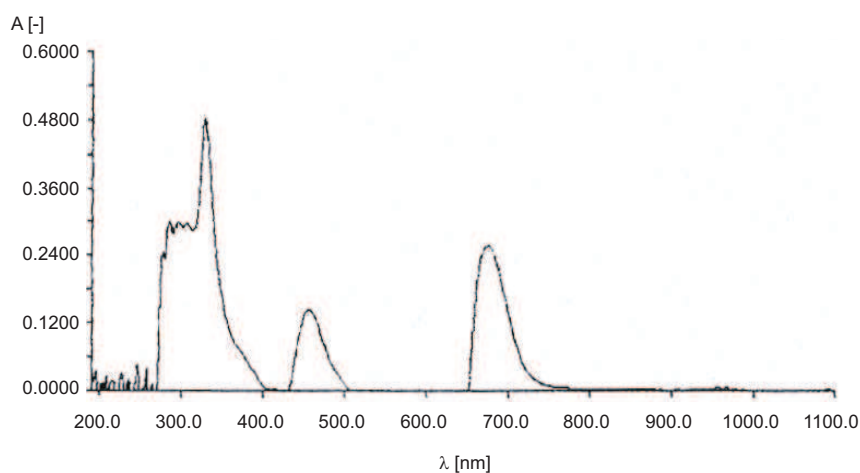


Fig. 2. Spectrophotometric spectra of the AgI_2^- - Brilliant Green complex

Calibration curve

The calibration curve was obtained using the above optimum experimental conditions and 10 calibration standards covering the range of 10 to 800 $\mu\text{g Ag}^+/\text{dm}^3$. Absorbance was a linear function of concentration over the range 10 to 800 $\mu\text{g Ag}^+/\text{dm}^3$, described by the equation $y = 0.00025x + 0.0432$ with $r^2 = 0.9973$. For better accuracy over the range 10 to 100 $\mu\text{g Ag}^+/\text{dm}^3$ the calibration curve covering this range is described by the equation $y = 0.0003x + 0.0391$ with $r^2 = 0.9758$.

Interferences

The interfering ions in the determination of Ag^+ were examined. Strong interference was exerted by the cations Hg^{2+} and Bi^{3+} with absorptions similar to that of Ag^+ . The cation Pt^{4+} did not interfere in concentrations up to 1 mg/dm^3 . The interference of the other cations is negligible. No interference was observed for cations such as Ba^{2+} , Sr^{2+} , Cu^{2+} and Sb^{3+} in concentrations up to 200 mg/dm^3 , Co^{2+} up to 500 mg/dm^3 , Ni^{2+} , Sn^{2+} , Zn^{2+} , Mn^{2+} , Ca^{2+} , Al^{3+} , As^{3+} , Fe^{3+} and Cr^{6+} up to 1000 mg/dm^3 , K^+ , Na^+ , Li^+ , NH_4^+ and Mg^{2+} up to $10\,000 \text{ mg/dm}^3$. From the anions, PO_4^{3-} up to 500 mg/dm^3 and NO_3^- , Cl^- , Br^- , F^- , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$, CO_3^{2-} and HCO_3^- up to 5000 mg/dm^3 did not interfere.

Application

The proposed method was applied to silver determination in a photographic fixing solution after processing a black white film. The sample was analyzed spectrophotometrically and by Atomic Absorption Spectrometry (AAS) which served as a reference value. The relative error of this method calculated as $\text{Er}\% = (\text{Ag}^+ \text{ found spectrophotometrically} - \text{Ag}^+ \text{ found by AAS}) \cdot 100 : (\text{Ag}^+ \text{ found by AAS})$ was found to be 4 %.

Conclusion

A new spectrophotometric determination of Ag^+ is proposed. The absorbance of the complex which is formed with an excess of I^- and Brilliant Green is observed at $\lambda = 680 \text{ nm}$. The linear range is from $10\text{--}800 \mu\text{gAg}^+/\text{dm}^3$. This proposed method is very simple, no extractions are needed, and it is of low cost. The method can be applied in photographic fixing baths and the results are reliable and comparable to those obtained by the AAS method.

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SPEKTROFOTOMETRYCZNE OZNACZANIE SREBRA ZA POMOCĄ ZIELENI MALACHITOWEJ W UTRWALACZACH FOTOGRAFICZNYCH

Abstrakt: Wykorzystując reakcję pomiędzy AgI_2^- a zielenią malachitową opracowano metodę prostego spektrofotometrycznego oznaczania srebra w roztworach wodnych. W odpowiednich warunkach w wyniku reakcji powstaje kompleks złożony absorbujący przy $\lambda = 680 \text{ nm}$. Stężenie jonów srebra można zadowalająco

oznaczyć w liniowym zakresie $y = 0,00025x + 0,0432$ z $r^2 = 0,9973$, od 10 do 800 $\mu\text{g Ag}^+/\text{L}$. Zbadano wpływ czynników przeszkadzających na wynik analizy. Proponowana metoda okazała się skuteczna w oznaczaniu srebra w utrwalaczach fotograficznych odprowadzanych do środowiska, a błąd względny tej metody wynosi 4 %.

Słowa kluczowe: srebro, zieleń malachitowa, oznaczenia spektrofotometryczne, roztwór fotograficzny