FACILE PHOTOMETRIC DETERMINATION OF SILVER WITH 2,4,5,7-TETRAIODOFLUORESCEIN STABILIZED WITH STARCH

ANALISIS FOTOMETRIK SEDERHANA KANDUNGAN PERAK DENGAN 2,4,5,7-TETRAIODOFLUORESCEIN YANG DISTABILISASI DENGAN KANJI

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ABSTRAK

Penentuan kadar perak dalam bahan uji menggunakan metode fotometrik secara sederhana telah dikembangkan. Dalam metode ini, 2,4,5,7-tetraiodofluorescein (erythrosine) dimanfaatkan sebagai reagen kromogenik untuk membentuk koloid positif dengan ion perak, tidak sebagai ion asosiasi sebagaimana diperkirakan pada awalnya. Koloid ini selanjutnya distabilkan dengan kanji dan sistem terner erythrosine-perak-kanji lebih lanjut dijadikan sebagai dasar dalam penentuan kadar perak dalam jumlah runut (0–6 µg/ml). Metode ini telah digunakan untuk menentukan kandungan perak dalam tiga bahan uji sintetik dengan akurasi > 96,87% setelah dibandingkan dengan hasil analisis spektrofotometri serapan atom (AAS) dan presisi < 8,8 %.

Kata kunci*: penentuan fotometrik, perak, 2,4,5,7-tetraiodofluorescein, erythrosine.*

ABSTRACT

Simple photometric determination of silver was developped. The determination incorporated 2,4,5,7-tetraiodofluorescein (erythrosine) as chromogenic reagent to form positive colloid with silver ion, not ion associate as initially assume. The colloid was then stabilized with starch and this ternary system erythrosine-silver-starch was applied as basis in determination of trace amount of silver (0–6 µg/ml). The developped method was successfully applied to determine silver in three synthetic samples and came with accuracy > 96.87% after compared to atomic absorption spectrophotometry (AAS) results and reproducibility < 8.8%.

Keywords*:* photometric determination, silver, 2,4,5,7-tetraiodofluorescein, erythrosine.

INTRODUCTION

Silver (Ag) is an element which become an interest in geochemical[1] and environmental studies.[2] In geochemical studies the interest is directed toward the finding of new mineral resources while in environmental studies it is focused on elucidating the impact of human activity especially in silver and base metal mining. In laboratory, the samples obtained usually would be analyzed using atomic absorption spectrophotometer (AAS) or induced couple plasma spectrometer (ICP). AAS and ICP are generally favored due to their sensitivity and simplicity but notoriously expensive. Other method could be applied is spectrophotometry or photometry which sensitivity could be compared with the sensitivity of AAS method. In both geochemical and environmental studies this method is still widely applicable to determine trace concentration of certain elements due to several advantages e.g. cheap, easy to executed

directly in the field by relatively inexperienced operator.[3] These advantages are considered significant due to the increasing interest in these fields especially in developing and poor countries. In these countries environmental problems are still of majorn concern and exploration program to find new mineral resources are heavily encouraged, which in turn require a simple, cheap, and easily accessed analytical method.[4]

Several photometric methods to determine silver concentration in samples had been reported including 2-(2-quinolylazo)-5-diethylamino-aniline,[5] dithizone,[6] thio michler's ketone[7] and rhodanine[8] as chromogenic reagent. Cation complex between Ag(I) with 1,10-phenanthroline had been exploited to form ion associated with several acid dyes as chromogenic reagent including tetrabromophenolphthalein ethyl ester,[9] bromopyrogallol red,[10] rose bengal, and eosin.[11] However silver determination with these method need to be stabilized by surfactant (polyvinyl alcohol or Triton X-305 in eosin method) which are expensive and hard to obtain. Without these surfactant the pseudo-solution of ion associated formed tend to precipitate. Besides, the precipitation could be prevented by using non polar or organic solvent (dithizone and bromopyrogallol red method) which implied complicated procedure involving solvent extractions.

One of chromogenic reagent could be used in silver determination photometrically is 2,4,5,7-tetraiodofluorescein (erythrosine). This dye is belong to xanthene dye group as eosin, rose bengal, and bromopyrogallol red. It is assumed that erythrosine would form ion associate with Ag(I) without cationic complex formation as in the method stated before. Erythrosine-silver ion associated also tends to precipitate, but this could be prevented by addition of starch as simple protective colloid. The use of starch in spectrophotometric analysis almost exclusively as chromogenic reagent which involved the formation of free iodine, while the use of it as protective colloid is quite limited e.g. trace analysis of magnesium using titan yellow as chromogenic reagent.[12] Therefore in this paper, the possibilities of simple photometric method using erythrosine as chromogenic reagent to form ion associated with silver and starch as protective colloid would be presented.

RESEARCH METHOD

Deionised water was used throughout the experiment. Chromogenic reagent used was solution of 2,4,5,7-tetraiodofluorescein disodium salt (erythrosine) 0.02% (Gunacipta, Indonesia). Erythrosine stock solution (0.0004%) was prepared by transferring 2 ml of 0.02% erythrosine solution to 100 ml volumetric flask and dilute to mark with deionised water and homogenized. Silver nitrate, acetic acid, nitric acid, hydrochloric acid, sulphuric acid, and natrium hydroxide are obtained from Merck, Darmstadt (Germany) all in analytical grade. Silver standard solution 500 µg/ml was prepared by dissolving 0.394 g silver nitrate in 1 ml concentrated nitric acid and diluted in 500 ml volumetric flask and marked with deionised water. The mixture was homogenized and stored in dark place.

Starch solution 5% was prepared by mixing 500 mg starch with 5 ml deionised water to form starch suspension which added slowly to 70 ml boiling deionised water with continuous stirring and boiled for further 5 minutes. The boiled or hot deionised water was added to mark the volume to 100 ml, and the mixture was then homogenized. The starch solution is stable for one day only and had to be prepared prior to use.

The instrument used in this experiment was spectrophotometer UV/Vis Spectroquant NOVA 60 with 1 cm quartz cuvette, provided by Merck, Darmstadt, Germany. Atomic Absorption Spectrophotometer used to determine the silver content in samples was Shimadzu AA-630 Atomic Absorption Spectrophotometer in Laboratory of Analytical Chemistry, Department of Chemistry, Institute of Technology Bandung, Indonesia.

To determine the optimum condition a series of working solutions were prepared by transferred accordingly standard silver solution to 25 ml volumetric flask (the final silver concentration was 60 µg/ml), which then buffered by acetic acid-sodium hydroxide buffer (pH varied between 2–12.5). After that, starch solution (the volume varied between 1–5 ml) and erythrosine (the volume varied between 0.25–2 ml) were added

consecutively and the mixture was diluted to mark with deionised water and homogenized. The result could be measured its absorbance immediately using the spectrophotometer and 1 cm cuvette.

To choose the best wavelength in which the absorbance of chromogenic system was maximum, an absorbance measurement was executed to a working solution in wavelength range 340–810 nm. The working solution used contained 60 µg/ml Ag(I) and 0.32 µg/ml erythrosine. Correlation between wavelength and absorbance (absorption spectra) is shown in Figure 1. Based on the figure the maximum absorbance of silver-erythrosine system occurred at 550 nm. This wavelength would be used in silver determination in further experiments.

To construct the calibration curve, a series of working solution with different silver concentration (0–60 µg/ml) was prepared accordingly to the optimum condition (pH, starch and erythrosine concentration) and measured at 550 nm using 1 cm cuvette. The measurement of sample solutions used the same optimum condition and wavelength.

RESULTS AND DISCUSSIONS

The pH of working solution significantly influenced the stability of chromogenic system which was implied by absorbance value measured in working solutions with different pH (Figure 2) at wavelength 550 nm. The desired pH was achieved by adding acetic acid-sodium hydroxide buffer accordingly to working solution. Based on the Figure 2, the optimum condition occurred at pH 4.5. In the working solution with lower pH, erythrosine tended to bind hydronium ion than silver ion. This is shown by decreasing absorbance in 550 nm. The tendency of erythrosine to bind hydronium ion was due to its property as acid-base indicator. At lower pH, erythrosine would loss its color due to protonization of its quinonoid group (Figure 3). At higher pH, absorbance decreased, probably due to instability of silver-erythrosine-starch system which cause precipitation of ion associated. The pink-violet precipitate would then be expelled from solution and left the relatively clear solution with low absorbance.

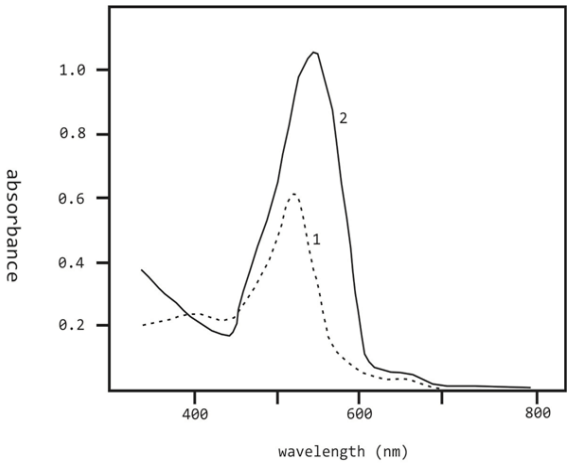

Figure 1. Absorption spectra of erythrosine (1), silver-erythrosine-starch chromogenic system(2).

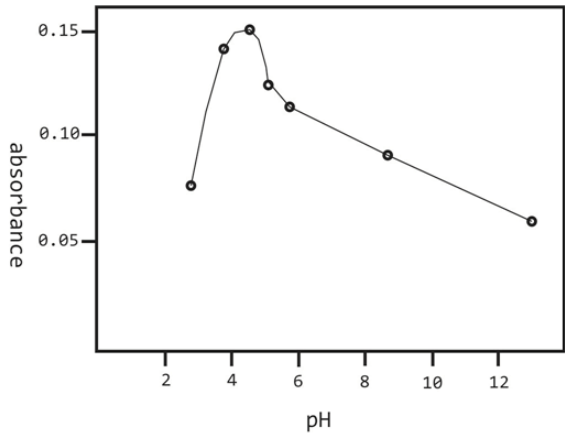

Figure 2. Correlation between pH and absorbance of silver-erythrosine-starch chromogenic system.

To study the effect of erythrosine concentration in the chromogenic system, a series of working solution was prepared with different erythrosine concentration, while silver and pH remained constant. The correlation between absorbance of chromogenic system and erythrosine concentration at wavelength 550 nm was shown in Figure 4. The concentration of erythrosine in the figure was represented by the volume of erythrosine stock solution added to working solution. Addition of 0.1 ml erythrosine stock solution (0.0004%) would bring its concentration 0.016 µg/ml in 25 ml working solution. Based on Figure 4, the absorbance reached the maximum when the erythrosine stock solution added to working solution was 1.5 ml. Addition of more erythrosine stock solution would decrease the absorbance due to instability of erythrosine-silver

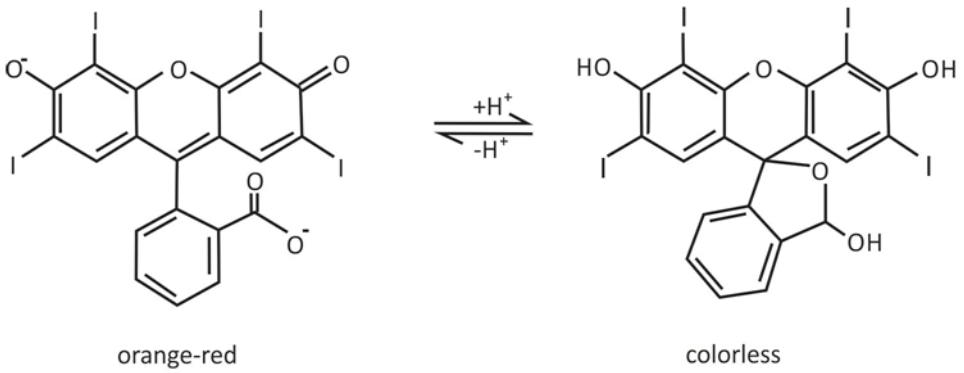

Figure 3. Protonation and deprotonation of erythrosine.

system which tend to precipitate, expelled from solution phase.

Molar ratio between silver-erythrosine in optimum condition was 134. This meant that a molecule of erythrosine attracted 134 silver ions. Based on the relatively great value of molar ratio, it was assumed that chromogenic system involved here was pseudosolution (colloid system) not ion associate as previously thought. It was also assumed that colloid system of silver-erythrosine was positive colloid due to the fact that it coagulated after addition of more negatively charged erythrosine ion (pink-violet precipitate and decreasing of absorbance).

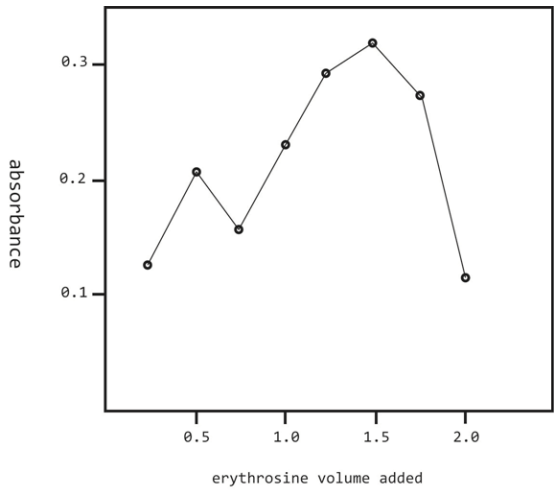

Figure 4. Correlation between absorbance and volume of erythrosine added to working solution.

In photometric method for inorganic analysis which phase measured was pseudosolution, a reagent had to be added to stabilize the chromogenic system to obtain homogenous phase and to ensure the accuracy and reproducibility of determination. Several reagents e.g. surfactant and protective colloid such as gum arabic and starch were frequently used. In this experiment starch would be applied as protective colloid to stabilize the pseudosolution of silver-erythrosine. To study the effect of starch to the chromogenic system, a series of working solution was prepared which silver and erythrosine concentration were remained constant (4 µg/ml and stock solution added 2 ml respectively). The volume of erythrosine added was 2 ml not 1.5 ml (optimum value based on Figure 4). This was done on purpose to see how effective the starch in preventing the coagulation. The acidity was kept constant (pH 4.5) using acetic acid-sodium hydroxide buffer. Starch added to 25 ml working solution varied between 0–5 ml and the result was shown in Figure 5. The figure showed that quantity of starch added correlated positively with absorbance until the volume of starch added was 2 ml, while after that the absorbance was relatively constant. Therefore, it could be deduced the optimum volume of starch added (2 ml).

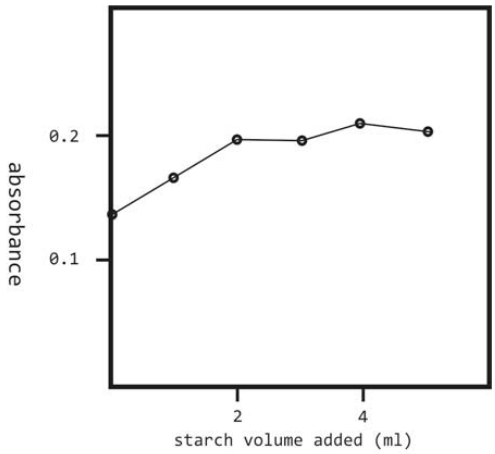

Figure 5. Correlation between absorbance and volume of starch added to working solution.

To determine the silver concentration in sample, a calibration curve had to be constructed to show the correlation between absorbance and silver concentration. A series of working solution with different silver concentration in optimum condition (amount of erythrosine and starch added, pH) was prepared accordingly to the general procedure. Absorbance was measured directly after homogenization using spectrophotometer at wavelength 550 nm. Figure 6 showed the calibration curve which absorbance and silver concentration could be represented by linear regression A = 0.0607 C + 0.3465 with correlation coefficient r = 0.988. A and C were absorbance and silver concentration in µg/ml respectively. Linear correlation occurred between 0–6 µg/ml silver. For silver concentration higher than 6 µg/ml, the calibration curve no longer fitted the linear equation. Molar absorptivity (ε) in this chromogenic system was $6.74 \cdot 10^3$ $molar^{-1} \cdot cm^{-1}$ with specific absorbance a = 0.062 $ml \cdot \mu g^{-1} \cdot cm^{-1}$.

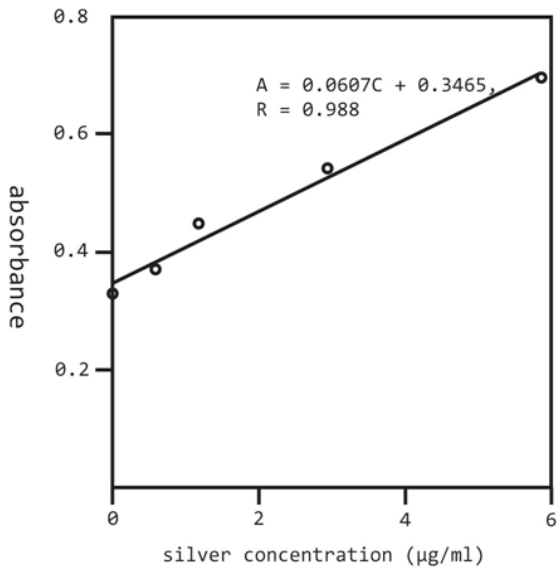

Figure 6. Calibration curve between silver concentration and absorbance (A = absorbance, C = silver concentration).

Study regarding the possibilities of interfering ions in this chromogenic systems had been carried out. Qualitatively alkaline, alkaline earth, and common transition metal ions such as Fe, Co, Ni, Zn, Cu, Pb, Hg, and Mn did not interfere in the determination. Only Zr (IV) so far was known to interfere severely by causing precipitation. From several anions tested (chloride, oxalate, EDTA, nitrate, and sulphate) only sulphate interfered by reducing the absorbance. To increase the selectivity it was highly advised to perform preconcentration and separation of silver as silver chloride precipitate.

The procedure had been applied to determine silver concentration in synthetic samples which sample matrix were obtained from acid digestion of soil samples. Each soil sample as much as 200 mg was digested by mixture of hot concentrated sulfuric, hydrochloric, and nitric acid until it was totally dissolved leaving only silica and silicate and evaporated to nearly dryness. The digestion results were then filtered using Whatman 41 filter paper and the filtrates were transferred to 50 ml volumetric flask, marked with deionised water, and homogenized. As much as 10 ml of the filtrate would be used as the matrix of synthetic samples. These synthetic sample was prepared by mixing 10 ml of the filtrate with a volume of silver nitrate with known concentration in 50 ml volumetric flask. White precipitate might occur and could be prevented by addition of concentrated hydrochloric acid. The mixture was then marked with deionised water and homogenized. In each analysis, 1 ml of the aliquot was transferred to 50 ml beaker glass, diluted to 5 ml with deionised water and boiled to nearly dryness. This was done to reduce the effect of strong acids which might present in the sample and to evaporate the chloride and sulphate introduced during soil sample digestion. The result was then transferred to 25 ml volumetric flask and the procedure followed referred to working solution preparation procedure (general procedure). As comparison, the synthetic samples were also analyzed using atomic absorption spectrophotometer Shimadzu AA-630 in Analytical Chemistry Laboratory, Department of Chemistry, Institute of Technology Bandung, Indonesia, which results were summarized in Table 1.

Based on Table 1, the determination of silver using the proposed method on three synthetic samples yielded suffice accuracy compared to AAS results which were set as true value. This was indicated by average recovery values which were close to 100%. Average recovery was ratio between proposed method and AAS method

Table 1. Results of silver determination in synthetic samples using photometric and AAS. Each sample was analyzed six times using proposed method and three times using AAS, the values shown here in silver found column were the mean values.

Samples	Silver Found (µg/ml)		Av. Recovery (%)	RSD (%)
	Proposed Method	AAS		
Sample-01	2.290	2.364	96.870	7.30
Sample-02	4.217	4.112	102.554	3.60
Sample-03	5.350	5.157	103.742	8.80

results. To determine the reproducibility, each sample was analyzed six times using the proposed photometric method and the results were shown in column relative standard deviation (RSD) which was ratio between standard deviation and mean value of silver found by proposed method. It could be seen that the RSD value were relatively low for moderate silver concentration and quite high for low and high concentration. This was due to increasing error for measurement close to detection limit. Besides, in order to increase the reproducibility, the condition between working solution used to construct the calibration curve (standard solution) and working solution contained samples should be strictly kept the same (pH, erythrosine, and starch concentration).

CONCLUSIONS

Erythrosine could be applied as chromogenic reagent in photometric determination of trace amount of silver (6 µg/ml). In this case erythrosine would bind silver ion to form positive colloid which could be stabilized by starch. This method could be applied as an alternative which technically and economically is more amenable.

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