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SPECTROPHOTOMETRIC METHOD FOR THE DETERMINATION OF SILVER USING 2,2',3,4-TETRAHIDROKSY-3'-SULFO-5'-NITROAZOBENZENE

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A fairly simple, selective and non-extractive spectrophotometric method for the determination of trace amounts of silver (I) was developed and 2,2',3,4-tetrahidroksy-3'-sulfo-5'-nitroazobenzene(TSNAB) suggested as a new analytical reagent for the direct non-extractive spectrophotometric determination of silver (I). In the aqueous medium TSNAB reacts with silver to give a highly orange absorbent chelate with a molar ratio of 1:2 (Ag: TSNAB). Note that the reaction is instantaneous and the maximum absorption was obtained at 490 nm that remains stable for 24 h. The average molar absorptivity and Sandell's sensitivity were found to be 1.37×10^4 l mol^{-1} cm^{-1} and 8.0 mkg cm^{-2} of silver(I) respectively. Linear calibration graphs were obtained for 0.864–5.184mkgml^{-1} of silver(I). A large excess of over 30 cations, anions and complexing agents impedes no determination. The non-extractive method is rather selective for silver(I) to have been successfully applied to synthetic mixtures.

Keywords: *spectrophotometry, silver, 2,2',3,4-tetrahidroksy-3'-sulfo-5'-nitroazobenzene, determination, synthetic mixtures.*

INTRODUCTION

Silver is a useful element in many respects. Silver is used in solar panels, water filtration, electrical contacts and conductors; specialized mirrors; catalysis of chemical reactions; a colorant in stained glass. Its compounds are used in photographic and X-ray film. Silver is both vital and toxic for many biological systems and its content in drink and tap water samples grows together with increased use of silver compounds and silver-containing products in industry and medicine. Of growing interest is the separation, pre-concentration and sensitive determination of silver ion.

1,5-Diphenylthiocarbazone is one of the most widely used photometric reagents to form colored water-insoluble complexes with silver ions. Silver-dithizone complexes are water insoluble and thus their determination requires a prior solvent extraction step into $CHCl_3$ or CCl_4, followed by spectrophotometric determinations [1]. In considering that these methods involve solvent, the extraction is lengthy, time-consuming and lacking selectivity due to excessive interference, $CHCl_3$ and CCl_4 have been listed as toxic. The problem has recently been resolved by suggesting a new analytical reagent for the direct non-extractive spectrophotometric determination of silver (I). The azocompounds on the basis of pyroghallol had widely been applied for the determination of noble metal ions, for this type of reagent has higher sensitivity and higher selectivity [2]. In the search for more sensitive azocompounds on the basis of pyroghallol reagent, the paper thoroughly analyzed a reagent 2,2',3,4-tetrahidroksy-3'-sulfo-5'-nitrorazobenzene

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(TSNAB) which was synthesized under the method of [3] and a color reaction of TSNAB with Ag(I) in aqueous media.

Although many sophisticated techniques, such as electro-thermal AAS [3], flame AAS [4], graphite furnace AAS [5], liquid chromatography [6] and electrophoresis [7] are used for the determination of silver at trace levels in numerous complex materials, factors such as the low cost of the instrument, easy handling, portable, lack of any requirement for consumables and practically no maintenance, have caused spectrophotometry to remain a popular technique, particularly in laboratories of eveloping countries with limited budgets.

The aim of the present study is to develop a simpler direct spectrophotometric method for trace determination of silver (I) with TSNAB in aqueous solutions. This method is far more selective, non-extractive, simple and rapid than all of existing spectrophotometric methods [9-12-8-11]. This method is very reliable and a concentration in the mkg m1^{-1} range in an aqueous medium at room temperature can be measured in a very simple and rapid way.

EXPERIMENTAL PART

Instrumentation

The absorbance of solutions was measured with a Perkin Elmer (United States) (Model: Lambda-40) double-beam UV/VIS spectrophotometer and with a KFK-2 photoelectrocolorimeter (Russia), with 1 cm matched quartz cells. The pH values of solutions were controlled on the ionomer İ-121 with a glass electrode customized by standart bufer solutions.

Chemicals and Reagents

2,2',3,4-tetrahidroksy-3'-sulfo-5'-nitrorazobenzene (2×10^{-3} M)

The reagent was synthesized according to the method of [2]. The solution was prepared by dissolving the requisite amount of bis-(2,3,4-trihidroksifenilazo) benzidine in a known volume of absolute ethanol. More dilute solutions of the reagent were prepared as required.

Standard silver solution (1×10^{-2} M)

A stock solution 1×10^{-2} M, 100 ml of silver(I) was prepared by dissolving 0.1575 g of silver nitratein 100 ml of distilled deionized water and added 0.1 ml con. HNO_3. The working standard of silver solution was prepared by suitable dilutions of this stock solution.

Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their analytical or equivalent grades and water soluble salts.

RESULTS AND DISCUSSIONS

Absorption spectra

The absorption spectra of orangecolor of the silver - TSNAB system in the presence of pH 9 solution were recorded using a spectrophotometer. The absorption spectra of the silver - TSNAB is a symmetric curve with maximum absorbance at 490 nm and an average molar absorptivity of 1.37 x 10^4 l mol^{-1} cm^{-1} and the reagent blank having maximum absorbance wave length at 380 nm. In all instances, measurements were made at 490 nm against a corresponding reagent blank.

Effect of acidity

Of the various pH 0-10of the solution studied, pH 9 was found to be the optimal for the silver - TSNAB system. The maximum and constant absorbance of the silver - TSNAB system was obtained in the presence of pH 9 at room temperature $(25\pm5)^0$C. The absorbance of the reagent solution and the silver - TSNAB system depends on the medium pH; therefore, the absorption spectra are studied relative to a blank experiment (TSNAB).

Effect of time

The reaction is fast. Constant maximum absorbance was obtained just after 5 min of the dilution to volume at room temperature (25 $\pm5^oC$), and remained strictly unaltered for 24 h.

Effect of temperature

The absorbance at different temperatures, 0–80°C, of a 25 ml solution of silver - TSNAB was measured according to the standard procedure. The absorbance was found to be strictly unaltered throughout the temperature range of 10–40°C. Therefore, all measurements were performed at room temperature (25 ±5°C).

Stoichiometry. The component ratio in the complexes was found using the isomolar series method, the relative yield method by Starik and Barbanel', and the equilibrium shift method. All the methods showed that the component ratio was 1 : 2 in the the silver - TSNAB system. The number of protons displaced upon complexation was determined by the Astakhov method, and the indicated component ratio in the complexes was confirmed [12].

Analytical performance of the method

Calibration curve

The effect of silver (I) concentration was studied over 0.01–10mkg l^{-1}, distributed in four different sets (0.1–10mkg l^{-1}) for convenience of the measurement. The absorbance was linear for 0.864 – 5.184mkg l^{-1} of silver (I) in aqueous media. From the slope of the calibration graph, the average molar absorption coefficient was found to be 1.37×10^4 l mol^{-1} cm^{-1} in aqueous media. The selected analytical parameters obtained with the optimization experiments are summarized in Table 1.

Table 1. Selected analytical parameters obtained by optimization experiments.

Parameters	Studied range	Selected value
Wave length /λmax (nm)	200- 800	490
pH	0 - 11	9
Time / h	1 - 24h	5 - 10 min
Temperature /°C	0 - 80°C	25±5°C
Me:R	-	1:2
Molar absorption coefficient / l mol^{-1} cm^{-1}	0.5×10^4-1.8×10^4	1.37×10^4
Linearrange/mkg l^{-1}	0.1-10	0.864-5.184
Detectionlimit /$mkgl^{-1}$	-	1
Sandell'ssensitivity /$mkgcm^{-2}$	-	8
RelativeStandard	0 -2	0 -2
RegressionCo-efficient	0.998-0.9999	0.999

Effect of foreign ions

The effect of over 30 cations, anions and complexing agents on the determination of only 1 $mkgml^{-1}$ of silver was studied. The criterion for interference was an absorbance value varying by more than 5% from the expected value for silver (I) alone. During interference studies, if a precipitate was formed, it was removed by centrifugation. The quantities of these diverse ions mentioned were the actual amounts studied but not the tolerance limit. However, for those ions whose tolerance limit has been studied, their tolerance ratios are mentioned in Table 2.

Table 2. Tolerance limits of foreign ions, tolerance ratio [Species(x)]/Ag (w/w)

Species x	Tolerance ratio [Species (x) /Ag (w/w)]	Reference[13]	Species (x)	Tolerance ratio, [Species (x) /Ag (w/w)]	Reference[13]
Na(I)	150	100	Au(III)	50	25
K(I)	150	10	Ga(III)	140	100
Mg(II)	180	100	La(III)	130	100

Ca(II)	160	20	Ta(IV)	140	100
Cr(III)	140	200	Ni(II)	165	100
Fe(III)	50	25	Pb(II)	130	100
Cu(II)	60	50	Cl^-	100	20
Cd(II)	80	50	HCO_3^-	180	100
Hg(II)	80	50	$C_2O_4^{2-}$	300	100
Mo(II)	145	100	EDTA	1500	1000
Co(III)	150	100	tartarat	1500	1000
Zn(II)	50	10	CH_3COO^-	1400	1000
Be(III)	140	50	Sr(II)	100	20
Sn(IV)	40	10	phosphate	150	100
Mn(II)	120	100	cyanide	120	50
V(V)	40	10	Al(III)	50	10

Precision and accuracy

The precision of the present method was evaluated by determining different concentrations of silver (I) (each analyzed at least five times). The relative standard deviation (n = 5) was 2%–0%, for 0.864–5.184mkg of Ag (I), indicating that this method is highly precise and reproducible. The detection limit (3s of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for Ag (I) were found to be 0.8mkg ml^{-1}. The reliability of our Ag-chelate procedure was tested by recovery studies. Regression analysis of Beer's law plots at 490 nm revealed a good correlation (R_2 = 0.999). The method was also tested by analyzing several synthetic mixtures containing silver and diverse ions (Table 3). The results for silver recovery were in good agreement with added values.

Applications

The present method was successfully applied for determination of silver in a series of synthetic mixtures of various compositions.

Determination of silver in synthetic mixtures

Several synthetic mixtures of varying compositions containing silver (I) and diverse ions of known concentrations were determined by the present method using EDTA as a masking agent and the results were found to be highly reproducible. The results are shown in Table 3. The accurate recoveries were achieved in all solutions.

Table 3. Determination of silver (I) in synthetic mixtures

	Composition of mixture (mkq/ml)	Siver(I) (mkq/ml)		Recovery ± s(%)
		Added	Found	
A	Ag^+	1.5 2.0	1.48 1.98	97±0.3 98±0.2
B	As in A + Cr^{3+} (25)+Fe^{3+}(25)	1.5 2.0	1.52 2.04	102±0.3 104±0.2
C	As in B +Mg^{2+} (25)+Hg_2^{2+} (25)	1.5 2.0	1.51 2.02	101±0.2 102±0.2
D	As in C + Co^{2+}(25)+ Ca^{2+} (25)	1.5 2.0	0.52 1.03	102±0.4 103±0.2
E	As in D +Cu^{2+}(25)+Ni^{2+} (25)	1.5 2.0	1.49 1.02	98±0.2 102±0.1

CONCLUSION

It is a new approach and alternative for the standard silver method (I). The present work provides that a simple, selective non-extractive and inexpensive method with silver - TSNAB system was developed for determination of silver (I) in samples for continuous monitoring to establish trace level of silver (I) in difficult sample matrices.

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SPEKTROFOTOMETRİK METODLA 2,2',3,4-TETRAHİDROKSİ-3'-SULFO-5'-NİTROAZOBENZOL (TSNAB) İLƏ GÜMÜŞÜN KİÇİK İZ MİQDARINININ TƏYİNİ

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Gümüşün(I) kiçik miqdarlarını təyin edilməsi üçün çox sadə, yüksək seçiciliyə malik və ekstraksiyasız spektrofotometrik üsul hazırlanıb. Yeni analitik reagent 2,2',3,4-tetrahidroksi-3'-sulfo-5'-nitroazobenzol (TSNAB) gümüşün(I) kiçik miqdarlarını birbaşa ekstraksiyasız spektrofotometrik təyin edilməsi üçün təklif olunub. Sulu məhlulda TSNAB gümüşlə reaksiyaya daxil olaraq 1:2 molar nisbətində sarımtıl-yaşıl xelat əmələ gətirir (Ag : TSNAB). Reaksiya sürətlidir, maksimal udma 490 nm-də müşahidə olunur və 24 saat ərzində sabit qalır. Gümüş (I) üçün işıqudmanın orta molyar əmsalı və Sendel həssaslığı 1.37×10^4 l/mol·sm və 8 mkq/sm^2 təşkil edir. Xətti dərəcəli qrafik gümüş (I) üçün 0.864-5.184 mkq/ml alınıb. 30-dan çox kation, anion və kompleks əmələgətirən agentlərin artıq miqdarı gümüşün təyin edilməsinə mane olmur. Metod gümüşə qarşı kifayət qədər həssasdır və bir sıra suni qarışıq nümunələri üçün uğurla tətbiq olunub.

Açar sözlər: *spektrofotometriya, gümüş, 2,2',3,4-tetrahidroksi-3'-sulfo-5'-nitroazobenzol, sintetik qarışıqlar.*

БЫСТРЫЙ СПЕКТРОФОТОМЕТРИЧЕСКИЙ МЕТОД ДЛЯ ОПРЕДЕЛЕНИЯ СЛЕДОВЫХ КОЛИЧЕСТВ СЕРЕБРА (I) С ИСПОЛЬЗОВАНИЕМ 2,2',3,4 –ТЕТРАОКСИ -3'- СУЛЬФО- 5'-НИТРОАЗОБЕНЗОЛА

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Разработан очень простой, высокоселективный и безэкстракционный спектрофотометрический метод определения следовых количеств серебра (I) с помощью нового аналитического реагента 2,2',3,4–тетраокси-3'-сульфо-5'-нитроазобензола (ТСНАБ). В водной среде ТСНАБ, реагируя с серебром, дает желтовато-зеленый хелат с молярным соотношением 1:2(Ag :ТСНАБ). Реакция быстрая и максимальное поглощение наблюдается при 490 нм и остается постоянной в течение 24 ч. Средний молярный коэффициент светопоглощения и чувствительность Сэндела для серебра (I) равны 1.37×10^4 л/моль·см и 8мкг/см^2 соответственно. Линейный градуировочный график получен в интервале 0.864-5.184мкг/мл. Избыток более 30 катионов, анионов и комплексообразующих агентов не мешают определению. Метод достаточно селективен по отношению к серебру и был удачно применен к ряду образцов.

Ключевые слова: *спектрофотометрия, серебро, 2,2',3,4 –тетраокси -3'- сульфо - 5'-нитроазобензол, определение.*