Spectrophotometric and Simultaneous Derivative Spectrophotometric Determination of Gold(III) and Silver(I) with Rhodanine Derivative in Micellar Medium

Abdel-Aziz Youssef El-Sayed
Department of Chemistry, Faculty of Science, Al-Azhar University, Assiout, 71511, Egypt

(Received March 3, 1994)

The determination methods of the gold(III) and silver(I) with, 5-(4-hydroxy-3-methoxybenzylidene) rhodanine (3,4-MHBR) in the presence of benzyldimethyltetradecylammonium chloride (zephiramine), and 5-(3,4-dihydroxybenzylidene) rhodanine (3,4-DHBR) in the presence of cetyltrimethylammonium bromide (CTAB) have been described. The application of first- and second-derivative spectrophotometry to simultaneous determination of gold(III) and silver(I) in their mixtures have been assayed using "zero-crossing" technique of measurement. In the pH ranges 8.8—9.8 and 9.0—10.2 the ternary 1 : 3 : 3 and 1 : 2 : 2 complexes gold(III)-3,4-MHBR-zephiramine and silver(I)-3,4-MHBR-zephiramine have been formed with molar absorptivities of 4.98×10^4 and 4.64×10^4 dm^3 mol^{-1} cm^{-1} at 529 and 522 nm, respectively. The ternary 1 : 3 : 4 and 1 : 2 : 3 complexes gold(III)-3,4-DHBR-CTAB and silver(I)-3,4-DHBR-CTAB have been formed in the pH ranges 9.4—10.2 and 9.0—10.5 with molar absorptivities of 8.63×10^4 and 7.76×10^4 dm^3 mol^{-1} cm^{-1} at 560 and 555 nm, respectively. The first- and second-derivative spectra of these complexes allow the determination of one metal in the presence an excess of the other. Gold(III) (0.21—3.6 μg cm^{-3}) and silver(I) (0.12—2.63 μg cm^{-3}) in different ratios have been determined simultaneously with good precision and accuracy using the proposed methods. The statistical analysis of the experimental results are presented. The methods have been applied to simultaneous determination of gold and silver in silicate rocks.

Derivative spectrophotometry was analytical technique of great utility and offers to simultaneously determination of two compounds in the same sample, without tedious and time-consuming separation procedures.[1—6] Simultaneous determination of gold and silver was hampered due to spectral overlap of their complexes. Derivative spectrophotometric technique was proved to be convenient and simple to resolve the problem of closely overlapping spectra by making use of the first- and second-derivative spectra of mixture.[7,8] 5-(*p*-Dimethylaminobenzylidene)rhodanine react with gold and silver ions in an acidic medium to form red complexes, which were sparingly soluble in water.[9,10] These complexes were either extracted into mixture of organic solvents,[9] or stabilized by protective colloids in aqueous medium.[10] However, these methods were very sensitive to reaction conditions and exhibits low sensitivities.[10] Azo-rhodanine[11] and pyridylrhodanine[12] derivatives were used for silver determination. However, their selectivities were low.

In the present paper, rapid, sensitive and selective methods for gold(III), silver(I) and their mixture determination have been proposed, in which rhodanine derivative containing hydroxyl groups were used as new reagents in the presence of cationic surfactants. The application of first- and second-derivative spectrophotometry to simultaneous determination of gold(III) and silver(I) with 5-(4-hydroxy-3-methoxybenzylidene)rhodanine (3,4-MHBR) and 5-(4-dihydroxybenzylidene)rhodanine (3,4-DHBR) in the presence of micellar medium were described using "zero-crossing" technique of measurement. The experimental conditions and statistical treatments of the experimental results were reported. The recommended procedures have been successfully applied to the simultaneous determination of gold and silver in silicate rocks.

Experimental

Reagents. All chemicals used of analytical grade and doubly distilled water was used for preparing the solutions. Standard gold solution, 1 mg cm^{-3}. Dissolve 0.1000 g of pure gold in 5 cm^3 aqua regia, evaporate the solution nearly to dryness. Add 2 cm^3 of concd hydrochloric acid, evaporate to half the volume, and dilute the solution with water to the mark in a 100-cm^3 standard flask. A working solution was prepared by dilution. Standard silver solution, 1 mg cm^{-3}. Dissolve 0.1575 g of dried (110 °C) silver nitrate in water containing 1 cm^3 of conc. nitric acid, and dilute the solution to the mark with water in a 100 cm^3-standard flask. 3,4-MHBR and 3,4-DHBR were synthesized according to Joulian and Sturgis.[13] 3,4-MHBR ethanolic solution, 1×10^{-3} M (M=mol dm^{-3}). Dissolve 0.0443 g of the reagent in ethanol by warming and dilute to the mark with the same solvent in a 250-cm^3 standard flask. 3,4-DHBR ethanolic solution, 1×10^{-3} M. Dissolve 0.0633 g of the reagent in 250 cm^3 of ethanol. Zephiramine solution, 1×10^{-2} M. Dissolve 3.54 g in water by warming and dilute to 1 dm^3 with water. CTAB solution, 1×10^{-2} M. Dissolve 3.64 g in 1 dm^3 water. Borate buffer solution. Dissolve ca. 19 g sodium tetraborate in 1 dm^3 water and then adjust the pH of solution with 1 M sodium hydroxide solution to desired value.

Apparatus. A Perkin–Elmer Model 3B double beam UV-visible Spectrophotometer equipped with 1-cm cells, controlled by Matsuba 386/33DX computer in conjunction with HP Laserjet 4L and HP Plotter-7574, was used for absorption measurements. Pecss Perkin–Elmer software program was used for obtaining the first- and second-derivative spectra and selection $\Delta\lambda$ (The auto-option uses a width which was the value calculated by the method of Savitzky and Golay[14]) at scan speed 120 nm min^{-1}. The pH measurements were carried out with an Orion Ionalyzer Model 920E with combined glass–calomel electrode.

Procedures. Determination of Gold(III) as 3,4-MHBR-Zephiramine Ternary Complex Using Zero-Order Spectrophotometry: Place a sample or standard solution containing less than 85 μg of gold(III) in a 25-cm^3 calibrated flask, add 3 cm^3 of 3,4-MHBR, 5 cm^3 of zephiramine and complete the volume to the mark with borate buffer of pH 9.6. Measure of absorbance after 20 min of mixing at 529 nm against a reagent blank. The calibration graph was prepared in the same manner.

Determination of Silver(I) as 3,4-MHBR–Zephiramine Ternary Complex Using Zero-Order Spectrophotometry: Place an aliquot of sample containing not more than 52.5 μg of silver(I) in 25-cm^3 calibrated flask. Add 3 cm^3 of 3,4-MHBR, 5 cm^3 of zephiramine and complete the volume with borate buffer of pH 9.6. Measure the absorbance after 20 min of mixing at 522 nm against a reagent blank.

Simultaneous Determination of Gold(III) and Silver(I) as 3,4-MHBR-Zephiramine Ternary Complexes Using First- and Second-Order Derivative Spectrophotometry: Place a sample or standard solution containing 2.0—85 μg of gold(III) and 1.5—52.5 μg of silver(I) in a 25-ml calibrated flask, add 3 ml of 3,4-MHBR, 5 ml of zephiramine and complete the volume with borate buffer of pH 9.6. Record the derivative spectra from 600 to 450 nm against a reagent blank. Measure the absolute values of the first derivative at 522 and 529 nm for the determination of gold(III) and silver(I), respectively. The corresponding values of the second derivative at 540 and 509 nm, respectively.

Determination of Gold(III) as 3,4-DHBR-CTAB Ternary Complex Using Zero-Order Spectrophotometry: Transfer a sample or standard solution containing less than 55 μg gold(III) in a 25-cm^3 calibrated flask, add 3 cm^3 of 3,4-DHBR, 5 cm^3 of CTAB and complete the volume with borate buffer of pH 9.8. Measure the absorbance after 30 min of mixing at 560 nm against a reagent blank.

Determination of Silver(I) as 3,4-DHBR-CTAB Ternary Complex Using Zero-Order Spectrophotometry: Transfer a sample or standard solution containing less than 31.2 μg of silver(I) in 25-cm^3 calibrated flask, add 3 cm^3 of 3,4-DHBR, 5 cm^3 CTAB and complete the volume with borate buffer of pH 9.8. Measure the absorbance after 30 min of mixing at 555 nm against a reagent blank.

Simultaneous Determination of Gold(III) and Silver(I) as 3,4-DHBR-CTAB Ternary Complexes Using First- and Second-Order Derivative Spectrophotometry. Transfer a sample or standard solution containing 1—55 μg of gold(III) and 1—31.2 μg of silver(I) in a 25-cm^3 calibrated flask, add 3 cm^3 of 3,4-DHBR, 5 cm^3 of CTAB and complete the volume with borate buffer of pH 9.8. Record the derivative spectra from 650—450 nm against a reagent blank. Measure the absolute values of the first derivative at 556 and 560 nm for the determination of gold(III) and silver(I) respectively, and the corresponding values of the second-derivative at 548 and 573 nm, respectively.

Results and Discussion

Preliminary experimentals have been conducted to investigate the influence of surfactants and protective colloids on the absorbance of the binary complexes formed by reactions of 3,4-MHBR and 3,4-DHBR with gold(III) and silver(I) ions. Maximum sensitization of these complexes were obtained in the presence of cationic surfactants. Zephiramine was optimum sensitizer for the color gold(III)- and silver(I)-3,4-MHBR complexes whereas, maximum enhancement of the absorbance of gold(III)- and silver(I)-3,4-DHBR complexes were obtained in the presence of CTAB.

Absorption Spectra. Figure 1 shows the absorption (zero-order) spectra of ternary (A) gold(III)-3,4-MHBR-zephiramine, with maximum at 529 nm, (B) silver(I)-3,4-MHBR-zephiramine, with maximum at 522 nm, (C) a mixture of gold(III) and silver(I) complexes, with a maximum at 525, i.e., between the absorption maxima of two components, and (D) 3,4-MHBR reagent in the presence of zephiramine, with a maximum at 475 nm. The absorption spectra of ternary (E) gold(III)-3,4-DHBR-CTAB, with a maximum at 560 nm, (G) silver(I)-3,4-DHBR-CTAB, with a maximum at 555 nm, (F) a mixture of gold(III) and silver(I) complexes, with a maximum at 557 nm and (H) 3,4-DHBR reagent in the presence of CTAB with a maximum at 495 nm are given in Fig. 2.

Optimization of Conditions for Complexes Formation. The effect of pH on the formation of gold(III) and silver(I) (3,4-MHBR and 3,4-DHBR)

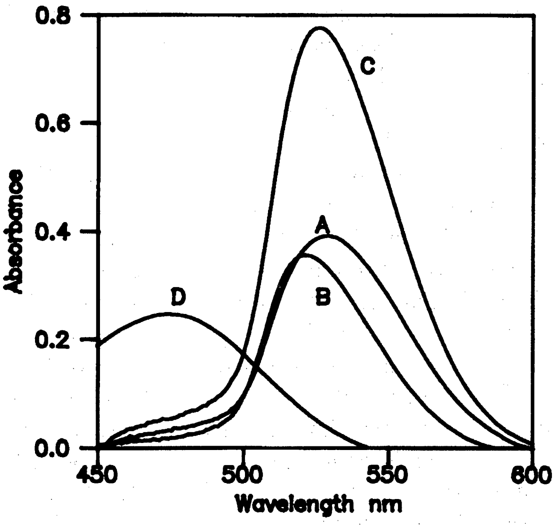

Fig. 1. Zero-order absorption spectra of (A) Au(III)-3,4-MHBR-zephiramine; (B) Ag(I)-3,4-MHBR-zephiramine; (C) mixture of Au(III) and Ag(I) ternary complexes; (D) 3,4-MHBR-zephiramine; [Au(III)]=1.6 μg cm^{-3}, [Ag(I)]=0.85 μg cm^{-3}; [Zephiramine]=2×10^{-3} M; [3,4-MHBR]=1.2×10^{-4} M for curves A, B, and C and 1.5×10^{-5} M for curve D. Reference: reagent blank.

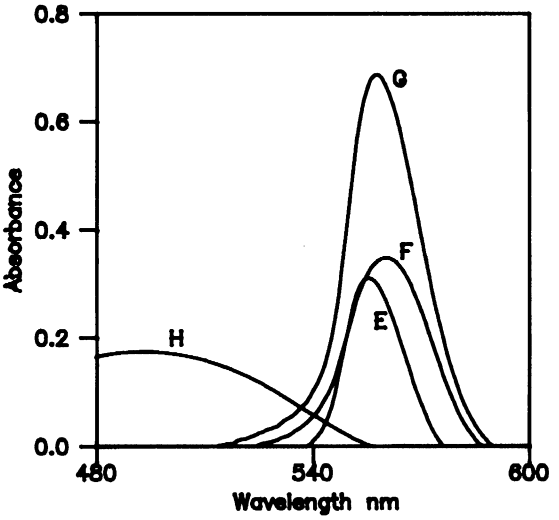

Fig. 2. Zero-order absorption spectra of (E) Au(III)-3,4-DHBR-CTAB; (F) Ag(I)-3,4-DHBR-CTAB; (G) mixture of Au(III) and Ag(I) ternary complexes; (H) 3,4-DHBR-CTAB; [Au(III)]=0.79 $\mu g\,cm^{-3}$; [Ag(I)]=0.43 $\mu g\,cm^{-3}$; [CTAB]=2×10^{-3} M; [3,4-MHBR]=1.2×10^{-4} M for curves E, F, and G and 4.5×10^{-6} M for curve H. Reference: reagent blank.

complexes in the presence of cationic surfactants were investigated using 8×10^{-6} M of gold(III) or silver(I), 1.2×10^{-4} M of 3,4-MHBR or 3,4-DHBR, and 2×10^{-3} M zephiramine or CTAB as the final concentration. The pH was adjusted with dilute hydrochloric acid or sodium hydroxide solution. The study revealed that maximum sensitivity of the gold(III) and silver(I) 3,4-MHBR-zephiramine complexes were obtained in the pH ranges 8.8—9.8 and 9.0—10.2, respectively. Therefore, pH 9.6 adjusted with borate buffer was selected to simplify the developed procedures for the spectrophotometric determination of gold(III) and silver(I) and simultaneous derivative spectrophotometric determination of their mixture. The corresponding pH ranges of gold(III)- and silver(I)-3,4-DHBR-CTAB complexes were 9.4—10.2 and 9.0—10.5. Consequently, pH 9.8 was recommended in the analytical procedures.

The optimum concentration ranges of 3,4-MHBR for the formation of gold(III) and silver(I) complexes in the presence of zephiramine were 8×10^{-5}—2×10^{-4} M and 6×10^{-5}—2.5×10^{-4} M, respectively. The corresponding 3,4-DHBR concentration ranges for the formation gold(III) and silver(I) complexes in the presence of CTAB were 4.5×10^{-5}—1.4×10^{-4} M and 5.5×10^{-5}—1.3×10^{-4} M, respectively. Thus 1.2×10^{-4} M (3 cm^3 of 10^{-3} M) 3,4-MHBR or 3,4-DHBR were selected in the recommended procedures.

A study of the influence of zephiramine concentration on the absorbance of the gold(III)- and silver(I)-3,4-MHBR complexes revealed maximum sensitization were obtained tin the presence of 8×10^{-4}—4×10^{-3} M and 1×10^{-3}—4.8×10^{-3} M of zephiramine. On the other hand, maximum sensitization of the gold(III)- and silver(I)-3,4-DHBR chelates were obtained in the presence of CTAB concentration $\geq9\times10^{-4}$ M. Therefore 2×10^{-3} M (5.0 cm^3 of 10^{-2} M) of zephiramine or CTAB was used throughout.

The absorbance of ternary gold(III)- and silver(I)-3,4-MHBR-zephiramine complexes increased during 10 min and then remained constant for 4 and 2 h, respectively. Thus standing time of 20 min was recommended in the procedures utilizing 3,4-MHBR as reagent. On the other hand, the ternary gold(III)- and silver(I)-3,4-DHBR exhibited maximum absorbance after 10 and 20 min, and then remained stable for 3 and 4 h, respectively. Therefore, absorbance measurements were carried out after 30 min of mixing.

First- and Second-Derivative Mode. Since absorption spectra of gold(III) and silver(I) complexes overlap (Figs. 1 and 2), their determination in mixture by conventional spectrophotometry was difficult. The measurement of the total absorbance of the mixture at two wavelengths of the maximum absorption and using simultaneous equations gives unacceptable results. In order to resolve this problem, the first- and second-derivative spectrophotometry have been applied.

The technique utilized to choice suitable wavelengths at which to take the measurements that were proportional to the gold(III) and silver(I) concentrations for the preparation calibration graphs was termed the "zero-crossing method". This technique involves measurement of the absolute value of the total derivative spectrum at an abscissa value (wavelength) corresponding to the zero-crossing point of the spectrum of the interfering component. Hence, measurements of the value of the derivative of a mixture, made at zero-crossing point of the derivative spectrum of one of the two components will be a function only of the concentration of the other component.

Figure 3 (a—d) shows series of first- and second-derivative spectra of mixtures by ternary gold(III)- and silver(I)-3,4-MHBR-zephiramine complexes. A series of first-derivative spectra of mixtures of 1.08 $\mu g\,cm^{-3}$ silver(I) plus increasing amounts of gold(III) (0.98—3.93 $\mu g\,cm^{-3}$) are given in Fig. 3(a). The corresponding second-derivative spectra are shown in Fig. 3(b). Figure 3(c) shows a series of the first-derivative spectra of mixtures of 1.97 $\mu g\,cm^{-3}$ gold(III) plus increasing amounts of silver(I) (0.54—2.1 $\mu g\,cm^{-3}$) whereas, the corresponding second-derivative spectra are given in Fig. 3(d). The heights h1 and h2 in the first-derivative spectrum of the mixtures corresponding to values taken at wavelength 522 nm (zero-crossing wavelength of gold complex) and 529 nm (zero-crossing wavelength of silver complex) were proportional to gold(III) and silver(I) concentration, respectively. In the second-derivative spectrum, the corresponding heights are h3 at 540 nm and h4 at 509 nm.

On the other hand, series of first- and second-deriva-

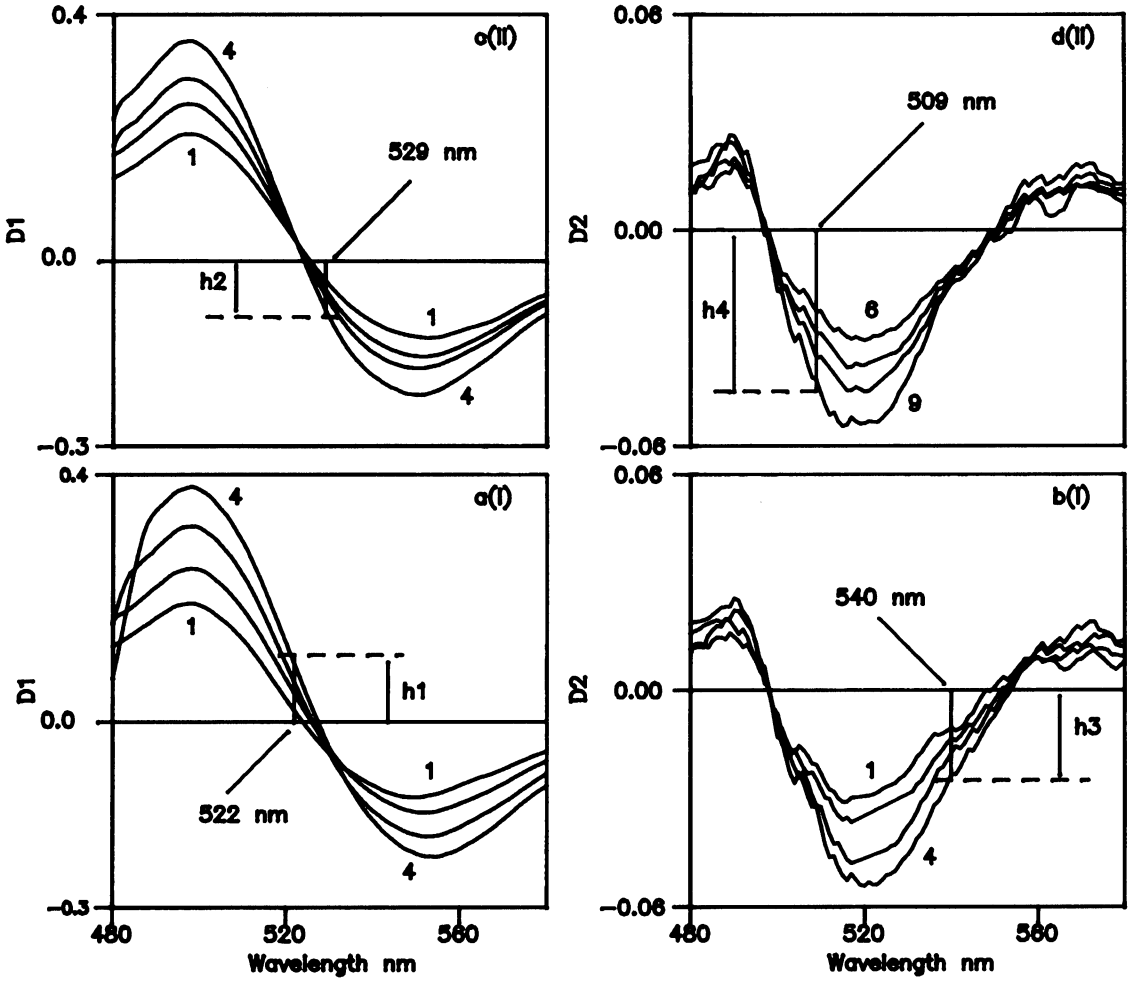

Fig. 3. First- and second-derivative spectra of mixture of ternary Au(III) and Ag(I)-3,4-MHBR-zephiramine complexes; (a,c) first- and (b,d) second-derivative spectra of (I) [Ag(I)]=1.08 μg cm^{-3}, [Au(III)]=0.98, 1.97, 2.95, and 3.94 μg cm^{-3} for lines 1, 2, 3, and 4, respectively and (II) [Au(III)]=1.97 μg cm^{-3}, [Ag(I)]=0.54, 1.08, 1.62, and 2.16 μg cm^{-3} for lines 6, 7, 8, and 9, respectively. Reference: reagent blank.

tive spectra of mixtures by ternary gold(III)- and silver(I)-3,4-DHBR-CTAB are shown in Fig. 4 (a—d), Figure 4(a) shows a series of first-derivative spectra of 0.69 μg cm^{-3} silver(I) and increasing concentration of gold(III) (0.31—1.89 μg cm^{-3}) whereas, the corresponding second-derivative are given in Fig. 4(b). A series of first-derivative spectra of mixture of 1.26 μg cm^{-3} gold(III) and increasing concentration of silver (0.17—1.0 μg cm^{-3}) are shown in Fig. 4(c). The corresponding second-derivative spectra are given in Fig. 4(d). The heights h1 at 556 nm (zero-crossing wavelength of gold complex) and h2 at 560 nm (zero-crossing wavelength of silver complex) in the first-derivative spectrum are found to be proportional to the gold(III) and silver(I) concentration, respectively. In the second-derivative spectrum, the corresponding heights are h3 at 548 nm and h4 at 573 nm.

Analytical Characteristics and Statistical Analysis. To obtain the linear calibration graphs passing through the origin for gold and silver determination, the recommended procedures were followed under the optimum conditions. The molar absorptivities (ε), linear-dynamic ranges, Sandell's sensitivities (S), regression equations, correlation coefficients, variance, and detection limits[7)] for gold(III)- and silver(I)-(3,4-MHBR-zephiramine and 3,4-DHBR-CTAB) system are illustrated in Table 1. From Table 1, it can be deduced that the developed methods for silver determination are more sensitive and simple than spectrophotometric methods utilizing 5-(p-dimethylaminobenzylidene) rhodanine ($\varepsilon=2.0\times10^4$ dm^3 mol^{-1} cm^{-1} at 450 nm)[10)] sulfochlorophenolthiopropiorhodanine ($\varepsilon=5.3\times10^4$ dm^3 mol^{-1} cm^{-1} at 535 nm)[11)] and 5-[4-(2-methyl-3-hydroxy-5-hydroxymethyl)pyridylene]rhodanine ($\varepsilon=1.5\times10^4$ dm^3 mol^{-1} cm^{-1} at 530 nm).[12)] Also, the suggested procedures for determination of gold are more sensitive and simple than the procedure utilizing 5-(p-dimethylaminobenzylidene) rhodanine in the presence of pyridine ($\varepsilon=3.8\times10^4$ dm^3 mol^{-1} cm^{-1} at 515 nm).[15)]

The calibration graph for simultaneous determination of gold and silver using 3,4-MHBR in the presence

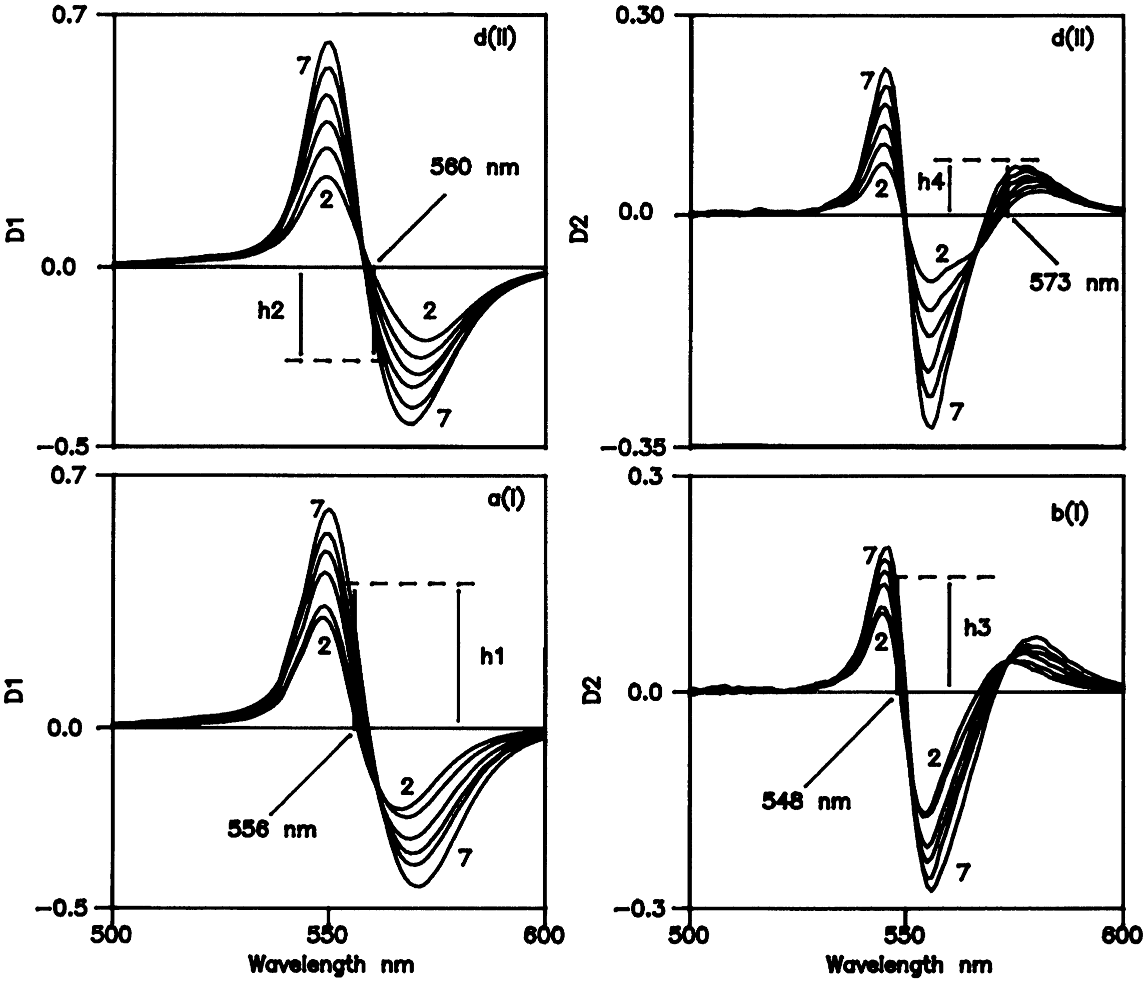

Fig. 4. First- and second-derivative spectra of mixture of ternary Au(III) and Ag(I)-3,4-DHBR-CTAB complexes; (a, c) first- and (b,d) second-derivative spectra of (I) [Ag(I)]=0.69 μg cm^{-3}, [Au(III)]=0.31, 0.63, 0.94, 1.26, 1.57, and 1.89 μg cm^{-3} for lines 2, 3, 4, 5, 6, and 7, respectively and (II) [Au(III)]=1.26 μg cm^{-3}, [Ag(I)]=0.17, 0.34, 0.52, 0.69, 0.86, and 1.03 μg cm^{-3} for lines 2, 3, 4, 5, 6, and 7, respectively. Reference: reagent blank.

Table 1. Analytical Characteristics and Statistical Analysis of the Determination of Gold and Silver by Zero-Order Spectrophotometry. Number of Standard Specimens, n=15, 99% Confidence Level

Ion	Reagent	λ nm	$\varepsilon \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}	Linear dynamic range μg cm^{-3}	S μg cm^{-2}	Regression equation[a)]	Corr. coeff.	Variance S_o^2	Detection limit μg cm^{-3}
Au(III)	3,4-MHBR	529	4.98	0.08—3.4	0.0039	A=0.25C+0.004	0.9998	2.09×10^{-5}	0.052
	3,4-DHBR	560	8.63	0.04—2.2	0.0023	A=0.44C+0.002	0.9999	2.58×10^{-5}	0.033
Ag(I)	3,4-MHBR	522	4.64	0.06—2.1	0.0023	A=0.43C+0.008	0.9997	1.51×10^{-5}	0.026
	3,4-DHBR	555	7.76	0.04—1.25	0.0014	A=0.72C+0.003	0.9999	1.42×10^{-5}	0.015

a) A, Absorbance; C, concentration (μg cm^{-3}).

of zephiramine were obtained from height (h) measurements in first- and second-derivative spectra for standards containing between 0.18 and 3.4 μg cm^{-3} of gold(III) in the presence of 1.08 μg cm^{-3} of silver(I). Similarly, the calibration graphs were prepared for standard containing between 0.06 and 2.1 μg cm^{-3} of silver(I) in the presence of 1.79 μg cm^{-3} of gold(III). On the other hand, the calibration graphs obtained by recommended procedures for simultaneous determination of gold and silver using 3,4-DHBR in the presence of CTAB were linear over ranges 0.14—2.2 μg cm^{-3} of gold(III) in the presence of 0.60 μg cm^{-3} of silver(I) and 0.05—1.25 μg cm^{-3} of silver(I) in the presence of 1.1 μg cm^{-3} of gold(III). The regression equations, correlation coefficients, variance, and detection limits are summarized in Table 2.

These results in Table 2, reveal that the amplitude of the derivative signal of the mixture at zero-crossing

Table 2. Statistical Analysis of the Determination of Gold(III) and Silver(I) in Mixtures by First- and Second-Derivative Spectrophotometry. Number of Standard Specimens, n=10, Confidence Level, 95%

Ion	Reagent	Derivative mode	λ / nm	Regression equation$^{a)}$	Corr. coeff.	Variance S_o^2	Detection-limit/ $\mu g\,cm^{-3}$
Au(III)	3,4-MHBR	1st derivative	522$^{b)}$	$D1=2.47\times10^{-2}C-6.05\times10^{-3}$	0.9955	2.76×10^{-6}	0.14
		2nd derivative	507	$D2=3.55\times10^{-3}C+1.5\times10^{-2}$	0.9880	8.95×10^{-6}	1.8
		2nd derivative	540$^{b)}$	$D2=4.37\times10^{-3}C+5\times10^{-3}$	0.9878	1.48×10^{-5}	1.9
	3,4-DHBR	1st derivative	556$^{b)}$	$D1=0.148C-2.15\times10^{-2}$	0.9917	9.25×10^{-5}	0.14
		2nd derivative	548$^{b)}$	$D2=6.40\times10^{-2}C-6.26\times10^{-3}$	0.9951	1.00×10^{-5}	0.11
		2nd derivative	565	$D2=5.69\times10^{-2}C-1.46\times10^{-3}$	0.9941	9.67×10^{-6}	0.12
Ag(I)	3,4-MHBR	1st derivative	529$^{b)}$	$D1=2.80\times10^{-2}C+1.48\times10^{-2}$	0.9789	5.51×10^{-5}	0.57
		2nd derivative	509$^{b)}$	$D2=1.17\times10^{-2}C+1.55\times10^{-2}$	0.9997	2.68×10^{-7}	0.09
		2nd derivative	555	$D2=4.20\times10^{-3}C-1.59\times10^{-4}$	0.9813	9.32×10^{-7}	0.49
	3,4-DHBR	1st derivative	560$^{b)}$	$D1=0.153C-1.24\times10^{-2}$	0.9870	1.55×10^{-4}	0.17
		2nd derivative	549	$D2=6.85\times10^{-2}C-1.14\times10^{-2}$	0.9554	1.12×10^{-4}	0.33
		2nd derivative	573$^{b)}$	$D2=6.03\times10^{-2}C-1.97\times10^{-3}$	0.9988	2.10×10^{-6}	0.05

a) D, Derivative value; C, concentration ($\mu g\,cm^{-3}$). b) Recommended for determination.

Table 3. Tolerance Limits for Diverse Ions in the Simultaneous Determination of Gold(III) and Silver(I) as 3,4-MHBR-Zephiramine Ternary Complexes Using Second-Derivative Spectrophotometry. Gold(III) 1.57 $\mu g\,cm^{-3}$, Silver(I) 0.86 $\mu g\,cm^{-3}$.

Diverse ion	Tolerance limit $\frac{[\text{Ion}]}{[\text{Au(III)}]}$	Tolerance limit $\frac{[\text{Ion}]}{[\text{Ag(I)}]}$
K^+,Na^+,NH_4^+,No_3^-,SO_4^{2-},Cl^-	>10,000	>10,000
Ba^{2+},Ca^{2+},Sr^{2+},Mg^{2+},Citrate, Tartrate, Malonate	4,000	5,000
Al^{3+},As^{5+},Be^{2+},Fe^{3+} $^{a)}$	2000	2000
Gd^{3+},La^{3+},Mn^{2+},Ni^{2+},Pr^{3+},U^{6+},Th^{4+}, EDTA	1000	1000
Cd^{2+},Cr^{3+},Mo^{6+},Pb^{2+},Sc^{3+},V^{5+},Zn^{2+}, Zr^{4+}	600	800
Sn^{2+},Ti^{4+}	400	500
H_2O_2	800	1000
NH_2–OH.HCl	500	200
Rh^{3+},Ru^{3+}	200	150
Pt^{4+} $^{c)}$	100	120
Pt^{4+},$^{c)}$ Cu^{2+} $^{a)}$	50	100
Hg^{2+},$^{b)}$ Pd^{2+} $^{c)}$		

a) 1.0 ml 0.25 M citrate–EDTA masking agent. b) 1.0 ml 0.1 M dithiocarbamate. c) 1.0 ml of 0.2 M dimethylglyoxime.

point of the derivative spectrum of one of the two components was function only of the concentration of the other component. Moreover, the high value of correlation coefficients, and intercepts on y-axis (close to zero) indicate the good linearity of all calibration graphs and conformity to Beer's law of first- and second-derivative measurements.

Composition of the Ternary Complexes. The molar-ratio and continuous variation methods were used at optimum pH's, to determine the metal : reagent ratio in the complexes, whereas, the iso-molar method[16] was utilized to determine the metal : surfactant ratio. These methods reveal the formation of 1 : 3 gold(III) : 3,4-MHBR (and 3,4-DHBR) complexes in the presence of zephiramine and CTAB, respectively. Moreover, the number of zephiramine$^+$ and CTA$^+$ associated with the formed complexes were 3 and 4, respectively. The ternary gold(III) complexes were probably $Au(3,4\text{-}MHBR)_3(Zeph^+)_3$ and $Au(3,4\text{-}DHBR)_3(CTA^+)_4$.

On the other hand, the metal : ligand ratio for silver(I)-3,4-MHBR (and 3,4-DHBR) were 1 : 2 in the presence of zephiramine and CTAB, respectively, whereas, the molar ratio of silver(I) to zephiramine$^+$ (and CTA$^+$) in silver(I) ternary complexes were 1 : 2 and 1 : 3 respectively. Therefore, the composition of these ternary complexes were $Ag(3,4\text{-}MHBR)_2(Zeph^+)_2$ and $Ag(3,4\text{-}DHBR)_2\ (CTA^+)_3$.

Effect of Diverse Ions. Effect of the presence of diverse ions in the simultaneous determination of gold(III) and silver(I) using 3,4-MHBR-zephiramine and

Table 4. Tolerance Limits for Diverse Ions in the Simultaneous Determination of Gold(III) and Silver(I) as 3,4-DHBR-CTAB Ternary Complexes Using Second-Derivative Spectrophotometry. Gold(III) 0.79 μg cm^{-3}, Silver(I) 0.43 μg cm^{-3}.

Diverse ion	Tolerance limit	
	[Ion] / [Au(III)]	[Ion] / [Ag(I)]
K^+,Na^+,NH_4^+,No_3^-,SO_4^{2-},Cl^-	>10,000	>10,000
Citrate,Tartrate, Malonate,F^-	6000	8000
Al^{3+},As^{5+},Be^{2+},Ca^{2+},Mg^{2+},Sr^{2+}	5000	6000
Mn^{2+},Ni^{2+},Fe^{3+} a)	4000	4000
Gd^{3+},La^{3+},Pr^{3+},U^{+6},Th^{+4},EDTA	1000	1000
Cd^{2+},Cr^{3+},Mo^{6+},Pb^{2+},Sc^{3+},V^{5+},Zn^{2+}, Zr^{4+}	600	800
H_2O_2	500	1000
NH_2–OH.HCl	1000	250
Rh^{3+},Ru^{3+},Pt^{4+}, c)Sn^{2+},Ti^{4+}	400	600
Cu^{2+}, a)Hg^{2+}, b)Pd^{2+} c)	80	120

a) 1.0 ml 0.25 M magnesium–EDTA masking agent. b) 1.0 ml 0.1 M dithiocarbamate. c) 1.0 ml of 0.2 M dimethylglyoxime.

Table 5. Simultaneous Determination of Gold and Silver as 3,4-DHBR-CTAB Complexes in Nile-Delta Silicate Rocks (Potassium Feldspar, $KAlSi_3O_8$) Using Second-Derivative Spectrophotometry

Sample	Weight	Certified μg g^{-1}		Found a)/μg g^{-1}			
	g	Au	Ag	Au	r.s.d/%	Ag	r.s.d/%
1	3.333	2	2	1.93	0.96	1.91	0.99
2	2.539	11	2	11.1	0.73	1.92	0.86

a) Average of five separate determinations.

Table 6. Simultaneous Determination of Gold and Silver as 3,4-DHBR-CTAB Complexes in River Water Sample Spiked with Gold(III) and Silver(I) Ions Using Second-order Spectrophotometry

Sample	Added/μg cm^{-3}		Found a)/μg cm^{-3}			
	Gold(III)	Siliver(I)	Gold(III)	r.s.d/%	Silver(I)	r.s.d/%
1	0.35	0.05	0.35	0.74	0.04	1.7
2	0.30	0.10	0.31	0.75	0.11	1.3
3	0.25	0.15	0.25	0.86	0.15	1.1
4	0.20	0.20	0.19	0.92	0.19	0.93
5	0.15	0.25	0.145	1.8	0.25	0.81

a) Average of five separate determinations.

3,4-DHBR-CTAB were studied using first- and second-derivative method. The transition metal ions and most common anions were tolerated even when present in large amounts. Tolerance limits of iron was increased by addition of citrate–EDTA and Mg–EDTA[17] as a masking agents (cf. Tables 3 and 4). When a precipitate appeared, it was removed by centrifuge before measuring the absorbance of the supernatant liquid. Absorbance measurement in the first- and second-derivative mode increased the tolerance limits of the noble metals to different extents in the presence of suitable masking agents. Tolerance limits of noble metals obtained using second-derivative method higher than first-derivative method. The tolerance limits (2% error maximum) are summarized in Tables 3 and 4.

Simultaneous Determination of Gold and Silver in Silicate Rocks [Nile Delta, Egypt]. The acid decomposition procedure of Van Loan and Borefoot[18] was followed by 1 g of the finely powdered sample into 50 cm^3 Teflon® beaker. Add 1 cm^3 of water to wet the sample. Then add slowly 10 cm^3 aqua regia. Add 10 cm^3 of hydrofluoric acid. Place the beaker on an oscillating hot plate at room temperature and allow the sample to dissolve (about 2 h). Evaporate the solution to dryness. Cool the sample, and the residue was extracted with ca. 20 cm^3 of 0.5 M sulfuric acid. The solution was evaporated to ca. 5 cm^3, cooled and transferred into 25 cm^3 volumetric flask. The procedures for simultaneous determination of gold and silver as 3,4-DHBR-CTAB using first- and second-derivative spectrophotometry were followed in the presence of 2 cm^3 of 0.25 M EDTA masking agent solution. When a precipitate formed, it was separated by centrifuge before measuring the absorbance of the supernatant solution. The relative standard deviation for gold determination in two silicate rocks samples were 2.7 and 1.84% with first-derivative mode and 0.9 and 0.73% with second-derivative mode. The corresponding values for silver were 2.8 and 2.11% with first-derivative method and 0.99 and 0.86% with second-derivative method. The results obtained using second derivative method have a better precision than the first-derivative method. The results are given in Table 5.

Simultaneous Determination of Gold and Silver Ion in River Water Sample. In drinking water, silver ions occur only as traces. Even if silver ions were added to water for the propose of germ inhibition,[19)] on the basis of silver's oligodynamic action, concentration were low (approximately between 0.03 and 0.1 $mg\,dm^{-3}$). The analyzed water sample were obtained from Nile river, Assiout city, Egypt. The water sample was concentrated either by extraction as Ag-dithizonate complex or by boiling.[19)] In neither the unconcentrated sample nor 100-fold concentrated sample could any gold or silver ion detected by atomic absorption spectrophotometry. Therefore, the river water was spiked with $\mu g\,cm^{-3}$ level of gold and silver ions and analyzed with the proposed procedures. The first and second-derivative procedure were successfully utilized for simultaneous determination of gold(III) and silver(I) as 3,4-MHBR zephiramine or 3,4-DHBR-CTAB complexes. However, the results obtained using second order derivative methods have a better precision. The results are illustrated in Table 6.

The author is grateful to Dr. H. S. Abdel Wahab, at the Department of Geology, Faculty of Science, Ain Shams University, for providing the sample of silicate rocks, and to Dr. F. Siegel, Professor of Geochemistry, George Town University, Washington, D. C. for conducting the reference analysis of these samples by neutron activation analysis (N. A. C, Toronto, Canada).

References

1) N. K. Agnihotri, H. B. Singh, R. L. Sharma, and V. K. Singh, *Talanta*, **40**, 415 (1993).

2) J. J. B. Nevado and C. G. Cabanilla, *Talanta*, **39**, 547 (1992).

3) M. Blanco, J. Coello, F. Gonzalez, H. Iturriaga, and S. Maspoch, *Anal. Chim. Acta*, **226**, 271 (1989).

4) S. Kus and Z. Marczenko, *Analyst*, **112**, 1503 (1987).

5) N. Suzuki and R. Kuroda, *Makrochim. Acta*, **11**, 47 (1987).

6) A. Bermejo-Barrera, M. P. Bermejo-Barrera, M. M. Guisasola-Escudere, and F. Bermegjo-Martinez, *Analyst*, **112**, 481 (1987).

7) B. Morelli, *Analyst*, **113**, 1077 (1988).

8) F. Salinas and A. M. Pana, *Analyst*, **112**, 1391 (1987).

9) R. Borissova, *Talanta*, **22**, 797 (1975).

10) R. Borissova, M. Koeva, and E. Topalova, *Talanta*, **22**, 791 (1975).

11) R. F. Gur'eva, L. M. Trutneva, and S. B. Savvin, *Zh. Anal. Khim.*, **33**, 632 (1978).

12) R. E. Godoy and A. G. Perez, *Analyst*, **111**, 1297 (1986).

13) P. L. Julian and B. M. Sturgis, *J. Am. Chem. Soc.*, **57**, 1126 (1935).

14) A. Savitzky and M. J. E. Golay, *Anal. Chem.*, **36**, 1627 (1964).

15) I. E. Lichtenstein, *Anal. Chem.*, **47**, 465 (1975).

16) J. I. G. Alonso, M. E. D. Garcia, and A. Sanz-Medel, *Talanta*, **31**, 361 (1984).

17) J. Inczedy, "Analytical Applications of Complex Equilibria," Chichester, London (1976), pp. 339—340.

18) J. C. Van Loon and R. R. Barefoot, "Analytical Methods for Geochemical Exploration," Academic Press, Inc., New York (1989), p. 241.

19) W. Fresenius, K. E. Quentin, and W. Schneider, "Water Analysis," Springer-Verlag, Berlin, Heidelberg, and New York (1988), pp. 393—399.