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SPECTROPHOTOMETRIC DETERMINATION OF GOLD WITH AZIDE

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ABSTRACT

The formation of the tetraazidogold (III) ion is indicated by the mole ratio method and confirmed by an analysis for azide on an evaporated sample. A spectrophotometric method for the determination of gold is based on measuring the absorbance of the complex at 325 mμ in water, for gold alone, or at 330 mμ in an n-butyl alcohol extract. Factors which control color development, color stability, and extraction are discussed and the effects of common foreign ions are noted. From 1.5 to 5.3 p.p.m. give absorbances within the optimum range, though Beer's law is followed well beyond these limits.

Few methods for the spectrophotometric determination of gold have appeared since the review given by Sandell (10), most of which use organic reagents for color development. Phenyl α-pyridyl ketoxime has been used to extract and determine 4 to 10 p.p.m. of gold; four platinum metals, as well as a number of other transition metals, are tolerated in milligram amounts (11). Hydrazine and sulfurous acid have been substituted for stannous ion in coprecipitating gold with tellurium prior to its determination with rhodamine B (8). Chloropromazine has been used as a colorimetric reagent for 0.5 to 8 p.p.m. of gold; a large number of common cations are tolerated, but platinum and palladium interfere (7). Methyl violet forms a complex with gold which can be extracted by halocarbon solvents, allowing the determination of gold in the range from 0.4 to 1.4 p.p.m. in the presence of platinum (5). From 0.5 to 5 p.p.m. of gold can be determined with thiocyanate but a number of common cations, as well as platinum and palladium, interfere (4). The original bromide method has been modified by the introduction of trioctyl phosphine oxide as an extractant for gold into chloroform (6). The optimum range is from 6.7 to 33.2 p.p.m. and most of the heavy metals are tolerated.

The optical absorbance of the tetraazidogold (III) ion is made the basis here for the determination of gold in the optimum ranges from 38 to 127 μg. in 25 ml. of water, at 325 mμ, or from 15 to 53 μg. in an extract made with 10 ml. of n-butyl alcohol, at 330 mμ. The color is developed immediately and is stable for about 15 minutes in water and for about 8 minutes in the n-butyl alcohol extract. The color reagent, 1.0 M sodium azide, is stable for months. The platinum metals, exclusive of ruthenium and osmium, do not interfere in milligram amounts if gold is extracted and read in the alcohol phase.

EXPERIMENTAL

Apparatus. All absorbance measurements and spectral scans were made with a Beckman DU spectrophotometer equipped with a photomultiplier tube, using 1.00 cm. silica cells and, when necessary, 0.90 cm. silica cell spacers. A Beckman Model 76 expanded scale pH meter was used for all pH measurements. Separatory funnels with Teflon stopcocks were used to avoid grease contamination of the organic solvent.

Reagents. Gold sheet, containing less than 0.02% copper as the only impurity (spectrographic analysis), was dissolved in aqua regia, boiled with concentrated hydrochloric acid, heated just to fumes with perchloric acid, cooled, and made to volume to give a 0.1000 M gold stock solution. Aliquots of the stock solution were taken for gravimetric analysis by reduction of the gold with hydrogen peroxide; no gold was lost in the process of solution. The stock solution was 0.400 M in chloride, as shown by titration of the filtrate by Fajan's method, and 0.417 M in hydrogen ion, after allowing for the hydrogen ion formed by oxidation of the peroxide. Other gold solutions were prepared by dilution of the stock solution. The 10^{-4} M solution used in preparation of the calibration curves was made 0.12 M in hydrochloric acid and was remade every 5 days. All gold solutions were kept in the dark.

Practical grade sodium azide (Eastman) having a purity of 99.2%, as determined from the hydrogen ion consumed on oxidation with nitrite (2), was used to make 1.00 M and 0.1000 M solutions. Initially, the solutions were slightly turbid and colored, but on standing for two weeks they cleared and precipitates settled out. Spectrographic analysis showed that the precipitates contained aluminum, calcium, magnesium, and iron, but that only traces of aluminum and calcium remained in the solutions. These aged solutions were used, and no attempt was made to purify the salt by recrystallization with organic

solvents (9,13), since the metal impurities would probably follow. The azide concentrations remained constant during the precipitation, and are stable for at least three months.

A buffer was prepared by dissolving 1 mole of monosodium phosphate monohydrate (Baker and Adamson reagent) in 800 ml. of water, adjusting the pH to 6.00 with 10 M sodium hydroxide, and diluting to 1 liter. The platinum metals used were described in a previous paper (1). Reagent grade mercuric and silver nitrates and purified tellurium metal (Fisher) were used in the interference tests.

Preliminary Tests. The tetraazidogold (III) ion, which forms immediately in water, was found to be extracted from acid solutions into n-butyl alcohol, isoamyl alcohol, and diisopropyl ether; the complex is reduced to metallic gold at high pH. The n-butyl alcohol was selected because it permits the back-extraction of traces of the platinum metals which may accompany the gold. A high concentration of an indifferent salt, such as the phosphate buffer, prevents emulsification and effects a fast phase separation.

Procedure. Gold alone, in the optimum range from 38 to 127 μg., may be determined by reading the color directly in aqueous solution. Transfer to 25 ml. volumetric flasks an aliquot of the unknown and sufficient aliquots of the 10^{-4} M gold solution to define a calibration curve in the optimum absorption range. Add to each flask 2.5 ml. of 1.00 M sodium azide and 12.5 ml. of the pH 6.00 buffer, and dilute to volume. Obtain the absorbance values within 15 minutes of preparation, at 325 mμ, against a blank containing all components but gold.

Gold in the presence of the tolerated platinum metals is determined by extraction. Add the sample solution to a 125 ml. separatory funnel; add 5 ml. of the pH 6.00 buffer and 2 ml. of 1.00 M sodium azide and adjust the volume to 10 ml. Add 10.0 ml. of n-butyl alcohol and extract by shaking for 30 seconds.

Discard the aqueous layer and wash the organic phase by shaking for 30 seconds with 10 ml. of solution containing 5 ml. of the buffer and 2 ml. of the azide. Withdraw 4 ml. of the n-butyl alcohol layer with a spitzer and expel it into a 1.00 cm. absorbance cell through a small tuft of cotton supported on a micro-funnel. Measure the absorbance within 8 minutes, at 330 mμ, against a blank which has been carried through the same procedure. Obtain a calibration curve by carrying aliquots containing 15 to 53 μg. of gold through the same procedure. If gold alone is determined by the extraction procedure, back-washing of the organic phase is unnecessary for both the sample and the calibration aliquots.

RESULTS AND DISCUSSION

Precision. Beer's law is obeyed by both the extracted and unextracted solutions; the quantities for the optimum absorption range are 38 to 127 μg. in 25 ml. of water and from 15 to 53 μg. in the alcohol extract for 1.00 cm. cells. The volume of the organic phase increases during the extraction from 10.0 ml. to 10.9 ml. The absorptivity, based on the initial 10.0 ml., is 0.1321 ± 0.0017 (std. dev.) $p.p.m.^{-1}$ $cm.^{-1}$ or 0.1440 $p.p.m.^{-1}$ $cm.^{-1}$ based on 10.9 ml. The volume returns to 10.0 ml. during back-washing and the absorptivity is then 0.01297±0.0016 $p.p.m.^{-1}$ $cm.^{-1}$, indicating a loss of about 1.8% of the gold. The absorptivity of the aqueous solution without extraction is 0.1368 ± 0.00020. When the aqueous to organic volume ratio is increased from 1:1 to 3:1, the absorbance of the extract increases linearly at the rate of 1% for each 15% increase in volume ratio, due to the increasing loss of alcohol into the aqueous phase which is not compensated by an increasing amount of water in the alcohol.

Statistical summaries of the results obtained for the three types of solutions are given in Table I.

Table I. Reproducibility.

No. of samples	μg. gold Added	Found	Range	Std. dev. μg.
		Extracted; not back-washed		
2	9.85	9.9(2)	9.8(5) - 10.0(0)	---
3	19.70	19.9(5)	19.6(7) - 20.1(7)	0.26
4	29.55	29.7(5)	29.4(5) - 30.0(6)	0.28
5	39.40	39.0(4)	38.7(4) - 39.2(7)	0.23
5	49.25	49.1(6)	48.7(1) - 49.4(7)	0.34
4	59.10	58.6(8)	58.5(3) - 58.9(1)	0.23
3	68.95	68.3(5)	68.3(5) - 68.3(5)	0.00
2	78.80	78.9(2)	78.5(4) - 79.2(2)	---
Std. dev. pooled, $\Sigma(n - 1) = 20$: 0.30 μg.				
		Extracted; back-washed		
5	19.70	19.5(8)	19.3(5) - 19.9(7)	0.26
5	39.40	39.6(8)	38.5(5) - 40.2(5)	0.73
5	59.10	58.9(0)	58.2(1) - 59.2(1)	0.44
Std. dev. pooled, $\Sigma(n - 1) = 12$: 0.33 μg.				
		Not extracted		
5	39.40	39.1(0)	38.2(0) - 40.0(0)	0.62
5	78.80	78.7(8)	78.5(0) - 79.1(3)	0.26
5	137.9	138.(9)	138.(0) - 138.(9)	0.30
Std. dev. pooled, $\Sigma(n - 1) = 12$: 0.39 μg.				

Composition of the Complex. Figure 1 shows spectral scans in the near ultraviolet region of the gold azide complex in water and in n-butyl alcohol, taken against appropriate blanks. These blanks are, respectively, an aqueous solution containing all constituents except gold, and n-butyl alcohol equilibrated with such a solution. Scans of these blanks are also shown, read against the respective solvents. If the scans of the complex are continued into the visible region of the spectrum they show a gradual diminution in absorbance.

The mole ratio method of Yoe and Jones (14) was used at 2×10^{-4} M and 2×10^{-5} M gold and at azide to gold ratios from 1:1 to 8:1, in the region of maximum absorptivity. To suppress possible hydrolysis of the azido-gold ion, the pH was regulated with sodium hydroxide or perchloric acid to 4.07 ± 0.10 or 3.89 ± 0.14, respectively, for the two concentration levels. All solutions were made to 1.00 M with sodium perchlorate to maintain constant ionic strength and were read against blanks containing gold (III) chloride and sodium perchlorate at the same concentration and pH levels. Sharp breaks at a ratio of 4:1 azide to gold are shown in Figure 2 at the 2×10^{-4} M gold level, indicating negligible dissociation of tetraazidogold (III) ion. A similar set of curves at the 2×10^{-5} M gold level also shows sharp breaks, but at a slightly higher than 4:1 ratio. This is probably explained by the slow oxidation of azide by gold (III), so that the apparent ratio of azide to gold is higher than the true ratio. At 2×10^{-5} M, finely divided gold appears in less than half an hour at ratios less than 4:1 and within a few hours at ratios greater than 4:1. At higher concentrations the solutions are more stable for the corresponding ratios. All of the foregoing results could be interpreted to indicate the primary formation of diazidogold (I) ion by the reaction

$$AuCl_4^- + 4N_3^- = Au(N_3)_2^- + 4Cl^- + 3N_2$$

instead of the formation of tetrazidogold(III) ion.

The addition of sodium or potassium azide to gold (III) chloride has been reported to form explosive orange colored needles upon careful evaporation of the solution (3). No analysis was reported for the product, but it has been referred to as AuN_3 (12). Repetition of this preparation in the present work, using a ratio of 10:1 azide to gold, gave a similar product which readily redissolved in water. The solution had an absorption maximum at 325 mμ, indicating the presence of the same complex ion as above. Another preparation by evaporation at pH 7 using 4:1 azide to gold, was analyzed for azide (2). Ratios of 1:3.89 and 1:3.98 were obtained, indicating negligible oxidation of azide by gold (III). It appears that the earlier preparations gave sodium and potassium tetraazidogold (III) salts rather than gold (I) azide, and that the tetraazidogold (III) complex is the absorbing species used herein.

Color Development in Aqueous Solutions. In the following studies the pH, the gold concentration, and the azide concentration were held constant at 6.00, 39.4 μg. and 0.02 M, respectively, unless otherwise indicated. Absorbances were read at 325 mμ.

Effect of Azide Concentration. The color intensity is insensitive to changes in azide concentration provided that it is kept greater than 6×10^{-3} M. On decreasing the azide concentration to 2×10^{-4} M the color intensity decreases to 77% of its maximum value.

Effect of pH. The pH was varied from 1 to 9 by adjusting with either sodium hydroxide or perchloric acid, while maintaining the ionic strength at 1.00 with sodium perchlorate. The color intensity remains constant in the pH interval from 4.35 to 7.00, but decreases slightly outside of these limits. For example, the intensity decreases to 93% and 97% of its maximum value at pH 1.00 and pH 9.00, respectively.

Time Stability. A study of absorbance versus time was made over a 70 minute interval while exposing the sample continuously to the fluorescent lights in the work area, except during the time necessary to obtain the absorbance values. The color intensity decreases at the rate of 2% per 15 minutes of exposure. For this reason more samples should not be prepared than can be read in 15 minutes. If the developed samples are kept in the dark, the decrease is less than 2% in 1 hour.

Extraction and Color Development in n-Butyl Alcohol. For the following studies conditions were held constant at pH 6.00, 0.5 M phosphate buffer, 39.4 μg. gold, 0.2 M azide, and phase volume ratio of 1:1, unless otherwise indicated. Absorbances were read at 330 mμ.

Effect of Azide Concentration. The color intensity in the extracted phase remains constant for 0.1 M to 0.2 M azide in the aqueous phase, but decreases from the maximum value by 7% and 86% upon decreasing the azide concentration to 10^{-2} M and 10^{-3} M, respectively.

Effect of pH. Spectrophotometric examination of the aqueous phase indicates that at least 99% of the gold is extracted at pH 6.00. The color intensity does not change, when corrected for blank absorbance, in the pH interval from 2.7 to 7.1. At pH values lower than 2.7 the absorbance decreases; e.g., 93% of the maximum absorbance is found at pH 1.90. At high pH values the gold is reduced. The extracted blank has an absorbance which varies from 0.074 at pH 1.85 to 0.010 at pH 7.90, presumably due to hydrazoic acid. Use of the buffer in preparing both sample and blank eliminates the effect of this variance.

Time Stability. The color intensity decreases at the rate of 2% per 8 minutes in light, as described above, and less than 2% in 1 hour in the dark.

Effect of Foreign Ions. Gold is easily reduced to the metal and this property serves well to separate macro to semimicro amounts from gross quantities of other metals. Reduction and coprecipitation with tellurium is used to isolate and concentrate micro amounts (8,10). Because of the ease of this separation, an extensive list of diverse ions was not studied. If sulfurous acid and hydrazine are used for the reduction (8) and the precipitate is redissolved in aqua regia, only tellurium, silver, mercury, palladium, and platinum will follow as impurities (10). None of these elements interfere when present in 1 mg. quantities, using the extraction procedure with back-washing, even though the silver is precipitated as chloride and the tellurium is present as the dioxide at pH 6.00. Of the platinum metals in 1 mg. amounts, only osmium and ruthenium interfere, because gold is reduced to metal by azide in the presence of these elements. They may be removed either by tellurium or by volatilization (10).

The anions chloride, perchlorate, sulfate, and phosphate in 0.1 M concentrations do not interfere in either the direct or extraction procedures. Cyanide, a strong complexing agent for gold, must be absent. Nitrate interferes with the direct procedure because it absorbs strongly in the ultraviolet spectral region, but it does not follow gold in the extraction procedure when present in 0.1 M concentration.

LITERATURE CITED

(1) Clem, R. G., Huffman, E. H., Anal. Chem. 37, 86 (1965).

(2) Clem, R. G., Huffman, E. H., Ibid., in press.

(3) Curtius, T., Rissom, J., Prakt. Chem. 58, 304 (1898).

(4) Deshumukh, G. S., Tatwawadi, S. V., J. Sci. Ind. Res. 20B, 506 (1961).

(5) Ducret, L., Maurel, H., Anal. Chim. Acta 21, 74 (1959).

(6) Holbrook, W. B., Rein, J. E., Anal. Chem. 36, 2451 (1964).

(7) Kum-Tatt, L., Anal. Chim. Acta 26, 478 (1962).

(8) Onishi, H., Microchim. Acta 1, 9 (1959).

(9) Pepkowitz, L. P., Anal. Chem. 24, 900 (1952).

(10) Sandell, E. B., "Colorimetric Determination of Traces of Metals," 3rd ed., p. 494 ff., Interscience, New York (1959).

(11) Sen, B., Anal. Chim. Acta 21, 35 (1959).

(12) Sneed, M. C., Maynard, J. L., Brasted, R. C., "Comprehensive Inorganic Chemistry," Vol. 2 (J. W. Laist), p. 237, Van Nostrand, New York (1954).

(13) Taylor, A. C., Nims, L. F., J. Am. Chem. Soc. 60, 262 (1937).

(14) Yoe, J. H., Jones, A. L., Ind. Eng. Chem., Anal. Ed. 16, 111 (1944).

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FIGURE CAPTIONS

Figure 1. Absorption spectra of analytical species and blanks

(A) 2×10^{-5} M Au^{+3} in water; 0.10 M N_3^-; 0.50 M PO_4^{-3}; pH 6.00; readings vs. (D)

(B) n-butyl alcohol extract of solution as for (A) except 0.20 M N_3^-; readings vs. (C)

(C) n-butyl alcohol extract as for (B) without Au^{+3}; readings vs. solvent

(D) solution as for (A) without Au^{+3}; readings vs. water

All with 1.00 cm. cell.

Figure 2. Mole ratio plots

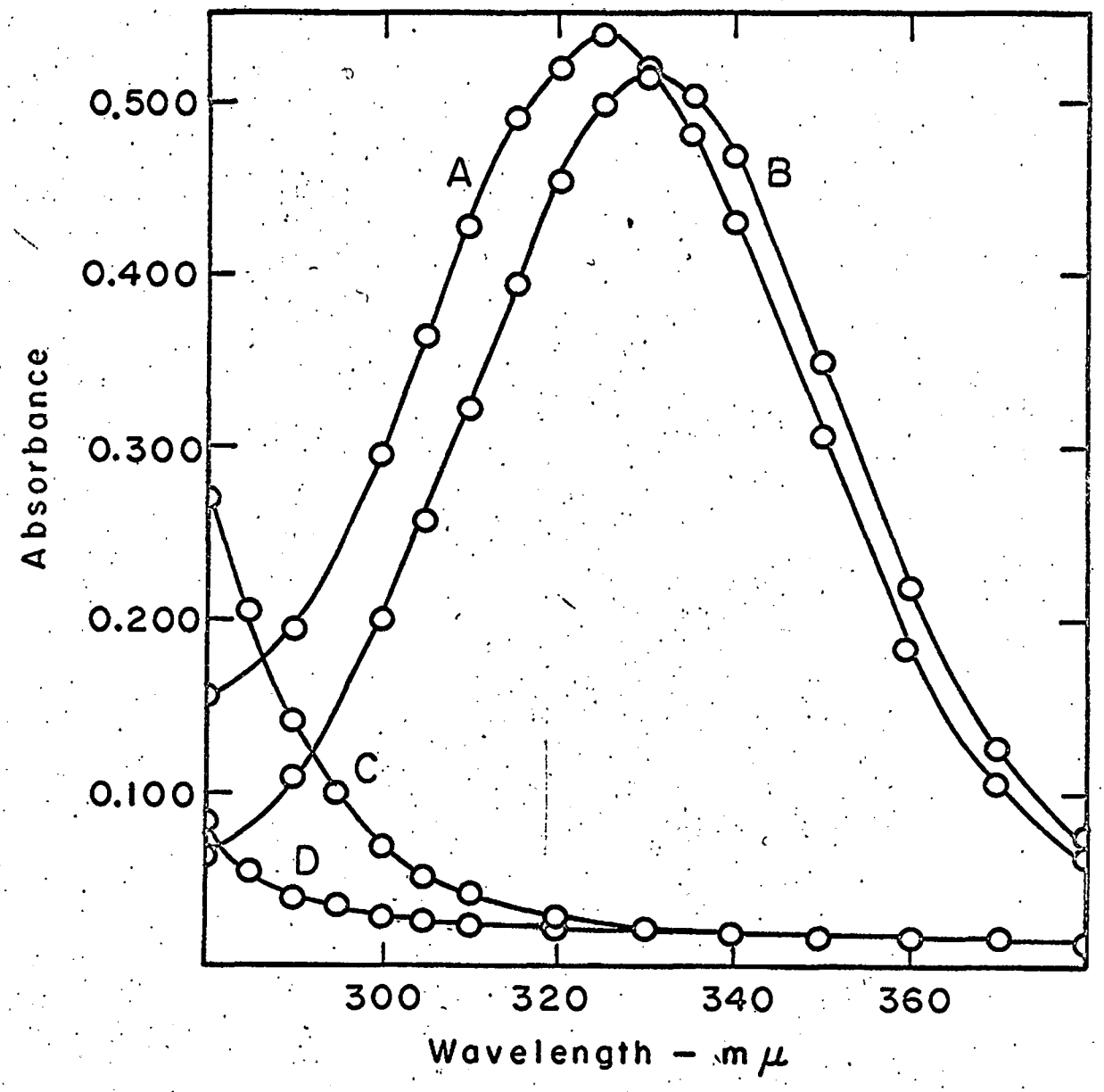
2×10^{-4} M Au^{+3}

2 to 16×10^{-4} M N_3^-

Ionic strength 1:00

pH 4.07 ± 0.10

0.10 cm. cell.


0.500
0.400
0.300
0.200
0.100
Absorbance
A
B
C
D
300
320
340
360
Wavelength – mμ

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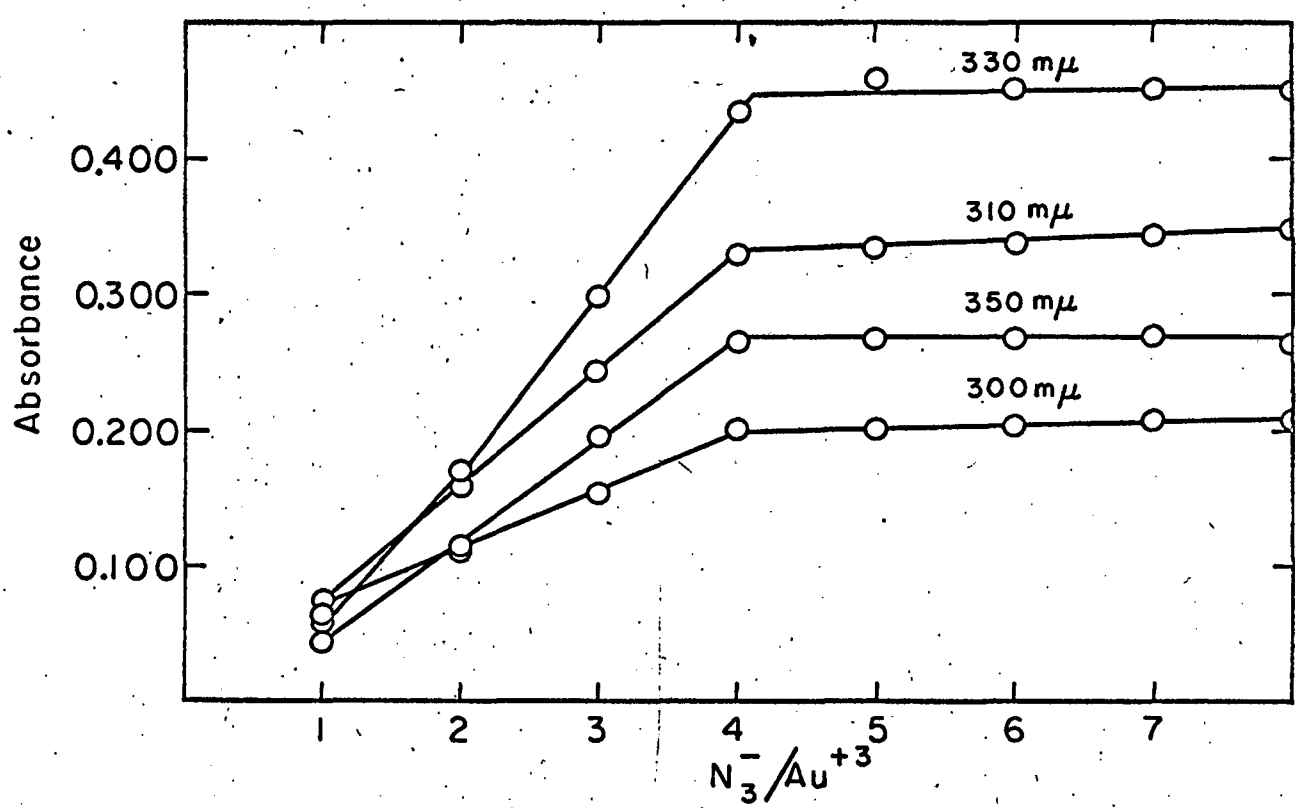
330 mμ
310 mμ
350 mμ
300 mμ
0.400
0.300
0.200
0.100
Absorbance
1
2
3
4
5
6
7
N_3^-/Au^{+3}

MUB-5225

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