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Spectrophotometric Determination of Gold(III) through Kinetic Reduction of Gold(III)-Gelatin Complex by Hydrazine in Aqueous Medium

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An aqueous solution of gold(III)-gelatin complex has been found suitable for the spectrophotometric determination of gold(III) in the range 0.6 μg ml^{-1} – 72 μg ml^{-1} after its reduction to a pink-coloured gold sol with hydrazine. The reduction is found to be first order with respect to [Au(III)complex].The pink coloured gold sol is fairly stable and exhibits molar absorptivity of 3.53×10^3 dm^{-3} mol^{-1} cm^{-1} at λ_{max} 530 nm in alkaline medium. The Sandell's sensitivity for an absorbance of 0.001, relative standard deviation and confidence limit (95%) for 10.30 μg of gold (50 replicates) are 5.58×10^{-2} μg cm^{-2}, 0.82% and 10.285 ± 0.021 respectively. The method shows a remarkable freedom from interferences.

Spectrophotometric methods for the determination of gold(III) generally involve binary complex formation between gold(III) ions and chromogenic reagents[1-5]; however, these methods lack sensitivity. Several extractants for the photometric determination of gold in complex materials have also been reported[6-10]. Conventional methods often involve lengthy procedures due to the necessity of multiple extractions[7], suffer from interference by other metal ions[4], or loss of photometric selectivity arising from the use of reagents such as amides[11], etc.

Long chain proteins have been commonly used for the suppression of polarographic maxima and more recently for the prevention of ion association[11]. This observation has prompted us to re-examine earlier application of gelatin[12,13]. We have now developed a simple and one-step procedure for the determination of gold(III) in water without the use of any toxic or expensive reagent. The various factors which affect the rate of reduction of gold(III)-gelatin have been determined. The method is very selective as well as sensitive and can be used in aqueous phase containing 50 diverse ions and can be applied to more dilute and biological samples without any degradation and pretreatment. Gold may also be reclaimed by this technique of reduction.

Materials and Methods

The absorbance measurements were carried out by the use of a Varian Carry-17D spectrophotometer with 1-cm quartz cell. The *p*H measurements were carried out with a ECIL digital 5652 *p*H meter. The numerical analyses were performed by a HP 1000 computer.

All the reagents used were of AR grade. $AuCl_3.xH_2O$ (1 g) (Johnson Matthey, London) was dissolved in sufficient amount of distilled water, the volume made upto 500 ml and was standardised by the quinol method[14]. A fresh stock solution of hydrazine was prepared by dissolving hydrazine sulphate (E Merck) in distilled water. The solution was then diluted to 10^{-3} *M*. Gelatin solution (1%) was prepared by dissolving gelatin powder (1 g) (Oxo Ltd, London) in 100 ml of warm distilled water. Owing to the obvious microbial degradation of gelatin and the aerial oxidation of hydrazine in water, both the solutions were prepared afresh before the estimation. The hydrazine solution was standardised[15] before use.

Procedure

Aliquots of aqueous solution containing variable amounts of Au(III) and 2 ml of (1%) gelatin solution were mixed together into a series of 10 ml calibrated flasks. The *p*H of the solution was adjusted to about 9.5 using 0.1 *M* NaOH solution. The solution was warmed to about 40°C for 2-3 min and then cooled to room temperature. Hydrazine sulphate solution was added so that the ratio of hydrazine: gold concentrations was 10:1. The mixture was then diluted to 10 ml with distilled water. After 150 min the absorbance was measured at 530 nm against water. For kinetic studies the absorbance values were recorded at different time intervals.

Results and Discussion

Gold(III)-gelatin interaction and effect of reducing agents

A coloured sol was formed by the gold(III)-amino acid complexes in the alkaline *p*H range but the sol particles could not be stabilised by the amino acids as such. However, the sol could be stabilised when carboxymethylcellulose solution was used in alkaline medium. The sol stabilisation property of carboxymethylcellulose solution is known previously[12] also. The complexation and stable coloured sol formation were observed with gold(III) and gelatin or gold(III) and egg albumin systems without adding amino acids. On the other hand, though carboxymethylcellulose solution stabilised the gold sol, the cellulose molecule was not suitable for binding gold(III) ions, like the protein molecules.

Gold(III) ions interact with gelatin in alkaline medium and produce colourless water-soluble gold(III) complexes, but complex formation is considerably affected by *p*H. Below *p*H 6.5, no gold(III)-gelatin complex results as is indicated by the expulsion of total gold(III) ions[12] through a dialysis bag at 30°C. But *p*H > 11.0 is not recommended, as gelatin solution would be hydrolysed at such a high *p*H. The binding of gold(III) ions with an amino group of gelatin may be of similar nature as described earlier[12]. Gold complexes of gelatin are expected to be reduced to gold metal by the strong reducing agents like hydrazine and ascorbic acid, etc. Ascorbic acid was successful in the production of sol at *p*H ~ 9.5, but it needed a longer reduction time as compared to hydrazine. The kinetic aspect of the reaction between gold(III)-gelatin complex and hydrazine was studied by simple spectrophotometric method. Stop flow technique[16] was not necessary in view of the comparatively slower reaction rate. The results were further corroborated by the expulsion of total anions, e.g., Cl^- or I^-, of uncomplexed $HAuCl_4$ or AuI_3 respectively through the dialysis bag at 30°C after the complexation of free gold(III) ions with gelatin. The results show that 1 ml of 1% gelatin can bind 1635 μg of gold(III) ions. Absorbance values were unaffected in the presence of a large excess of gelatin.

Absorption spectra

The particle size of the gelatin-stabilised gold sol was smaller when the reduction of Au(III)-gelatin solution was done at a *p*H above 9.5, but it was larger when reduction was done around *p*H 3.0. The reduction at a lower *p*H produced a blue sol solution (λ_{max} 560 nm) and that at higher *p*H resulted in a pink solution (λ_{max} 530 nm). In both the cases the Au(III)-gelatin complex has negligible absorbance. So, all measurements were done against water blank. The proposed spectrophotometric method gives a solution with a molar absorptivity of 3.53×10^3 l mol^{-1} cm^{-1}. The Sandell sensitivity for an absorbance of 0.001 is 5.58×10^{-2} μg cm^{-2}, with a relative standard deviation of 0.82% and a confidence limit (95%) of 10.285 ± 0.021 for 10.30 μg of gold (50 replicates).

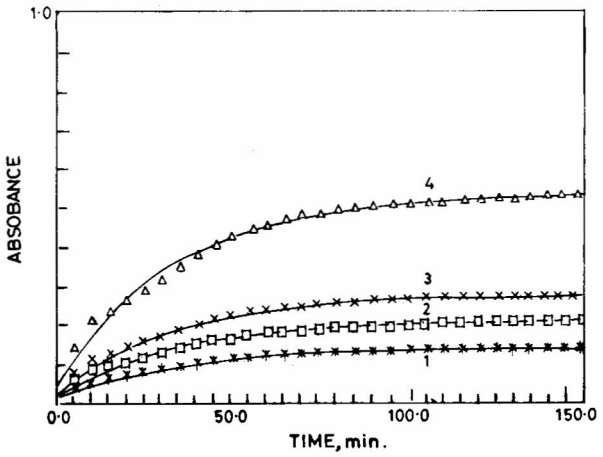

Fig. 1 – Absorbance versus time curves for the reduction of Au(III) to Au(0) by hydrazine (1) 7.9 μg/ml of Au, (2) 11.84 μg/ml of Au, (3) 15.81 μg/ml of Au, (4) 29.55 μg/ml of Au; *p*H 9.5; solid lines correspond to computer generated curves for the proposed kinetic path.

Reduction profile

The reaction rate is dependent on the temperature, but is independent of the concentration of Au(0) in solution. Kinetic analysis of the curve showed (Fig. 1) that the reaction was of first order with respect to the Au(III)-complex concentration in solution. For the first order reaction, monitored via absorbance changes, the absorbance versus time relationship is given by $A_t = A_\infty - (A_\infty - A_0)e^{-kt}$, where, A_0, A_t and A_∞ are initial, intermediate and final absorbances, and k and t are the first order rate constant and time. A computer programme in FORTRAN was developed to generate the change in concentration for each species. Linear regression analysis was used to estimate suitable value of K and A to match the experimental data[17,18]. It follows that the reduction of Au(III)-gelatin complex to Au(0) is a first order process. The K value is 0.0308 min^{-1}. The relationship between concentration and the computed absorbance changes was evaluated with

four solutions. The reaction profile was studied taking the advantage of the comparatively slower reduction rate.

Effect of pH and the sol particle

It was observed that for the quantitative reduction of gold-gelatin complex, a ten-fold excess of hydrazine was needed in the reaction media. The presence of anions, excess hydrazine (more than ten times the amount of gold) and the amount of gold-gelatin complex in the reaction media had no influence on the rate of the reduction reaction. The effect of *p*H on the reaction rate in solution containing 0.1184 mg of Au, 2 ml of (1%) gelatin solution and 1 mg hydrazine was investigated. The hydrogen ion concentration was changed from 1×10^{-6} to 10^{-11} *M* by the addition of NaOH solution. The reaction rate was essentially unaffected in the *p*H range of 9.0-11.0, and between *p*H 6.0 and 9.0 the anomalous absorbance indicated the irregular particle size of the gold sols. In the *p*H range 2.0-3.5 uniform but larger particle size (blue solution, λ_{max} 560 nm) of the gold resulted where gelatin remained only as a sol stabiliser but not as a complexing agent. Owing to the anomalous reduction phenomenon, *p*H-dependent kinetics was not studied. This was authenticated by the reduction of $HAuCl_4$ solution by hydrazine in carboxymethyl cellulose solution.

The time-dependent reduction of gold-gelatin complex with hydrazine was studied keeping all the other factors constant. It was observed that the reduction (99%) was complete only after 120 min but all measurements were done after 150 min.

To further classify the stability of the sol, experiments were performed at different temperatures. Analysis of the rate profiles showed a temperature-dependent reaction path. The temperature dependent reduction was studied at three temperatures (20°, 24° and 32°) showing the activation parameters, $\Delta H^* = 5.6$ kcal mol^{-1}, $\Delta S^* = -234$ JK^{-1}. At a temperature above 40°C, the decrease in absorbance values indicated that the destabilisation of the sol particle in aqueous medium may be due to the precipitation of gold metal by a sol aggregation process or by the denaturation of the polymer used. The gold-gelatin complex in alkaline solution remained stable in the temperature range 20°C – 40°C for a period of four weeks.

The effect of reasonable ionic strength on the reaction rate cannot be studied due to the coagulation of gold sol[13]. However, it has been observed that very low ionic strength (< 0.05 *M*) does not disturb the gold sol and the rate of reduction of gold(III)-gelatin complex.

Effect of diverse ions

Solutions containing 10.30 μg ml^{-1} of gold and various amounts of other ions were mixed and the recommended procedure for gold determination was followed. Alkali and alkaline earth metal ions along with As(III), Mn(II), Zn(II), Cd(II), Sn(II), Bi(III), F^-, Cl^-, NO_3^-, NO_2^-, CO_3^{2-}, SO_3^{2-} do not interfere when present in 500-fold excess. About 100-fold excess of Co(II), Ni(II), Cr(III), Al(III), Hg(II), Pt(II), 50-fold excess of Ag(I), Fe(II) and Fe(III), acetate, tartrate, citrate, 20-fold excess of H_2O_2, 5-fold excess of Cu(II), U(VI), Th(IV) and one-fold excess of Pt(IV), Ra(III), Ru(III), Pd(II), Os(VIII), Ir(III), Re(VII), Mo(VI), W(VI), La(III), V(V) and I^- can be tolerated. The interference due to H_2O_2 can be removed simply by boiling the gold solution before complexation with gelatin. Ba(II), Mn(II), Co(II), Ni(II), Hg(II), Pb(II) could be effectively masked by Na_2-EDTA solution. Therefore, the procedure is very simple, selective and the tolerance limits to diverse ions, except iodide and platinum(IV), are very high. However, the interference due to iodide can be removed effectively by dialysis. Two-fold excess of Ru(III), Rh(III), Os(VIII), Ir(III), Pd(II) and Pt(IV) was tolerated when the calibration curve for Au(0) sol was made at 560 nm after the reduction of Au(III)-gelatin complex at *p*H 2.0-3.5.

In order to confirm the usefulness of the proposed method it was applied to the determination of gold in three synthetic matrices and to a concentrate from low-grade gold ore, overcoming the influence of the interferents. The results are summarised in Table 1 together with the results ob-

Table 1 – Determination of Gold in Various Samples

Sample	Gold found by present method*	Gold found by AAS method*	Relative standard error, %
Synthetic samples (amounts added in mg)			
Au(17.7) + Cu(50) + Al(800) + Fe(100) + Rh(10) + Ir(7)	17.6 μg	17.6 μg	0.56
Au(14.16) + Pt(10) + Pd(10) + Cr(200) + Mn(800)	14.0 μg	14.1 μg	1.12
Au(10.3) + Os(10) + V(10) + Fe(100) + Co(500) + Ni(500)	10.26 μg	10.2 μg	0.38
Gold Ore (Au-0.0024%)	23.8 μg/g	23.6 μg/g	0.83

*Average of five determinations

tained by atomic absorption spectrometry, carried out for comparison. Gelatin-stabilised gold sol in alkaline medium is well suited for preconcentration, recovery and reclaiming of gold from low grade solutions, and platinum metal concentrate. The method is simple, reproducible and can be applied to dilute biological samples without any degradatgion and pretreatment.

References

1 Beamish F E & Van Loon J C, *Analysis of noble metals*, (Academic Press, New York), chapter 3, 1977.
2 Das H R & Bhattacharyya S N, *Talanta*, **23** (1976) 535.
3 Diamantatos A, *Anal chim Acta*, **66** (1973) 147.
4 Anuse M A, Mote N A & Chavan M B, *Talanta*, **33** (1983) 323.
5 Anuse M A, Kuchekar S R, Mote N A & Chavan M B, *Talanta*, **32** (1985) 1008.
6 Mirza M Y, *Talanta*, **27** (1980) 101.
7 Patil P S & Shinde V M, *Mikrochim Acta*, **II** (1973) 331.
8 Mojski M, *Talanta*, **25** (1978) 163.
9 Nesterenko P N & Lomonosov M V, *Zh anal Khim*, (1984) 456.
10 Patel K S & Lieser K U, *Analyt Chem*, **58** (1986) 1547.
11 Jaya S, Rao T P & Ramakrishna T V, *Analyst*, **108** (1983) 1151.
12 Pal T & Maity D S, *Analyst*, **111** (1986) 49.
13 Pal T & Ganguly A, *Analyst*, **112** (1987) 1327.
14 Vogel A I, *A text book of quantitative inorganic analysis* (Longman, London) 1973, pp. 464-465.
15 Pal T, Maity D S & Ganguly A, *Analyst*, **111** (1986) 1413.
16 Taquikhan M M & Martell A E, *J Am chem Soc*, **89** (1967) 4176.
17 Mieling E & Pardue H L, *Analyt Chem*, **50** (1978) 1611.
18 Rao C P, *Piecewise constant orthogonal functions and their application to systems and control* Lecture notes on Control and Information Sciences Series-55, Springer Verlag), 1983.