

Extraction Equilibrium and Simple Extractive Spectrophotometric Determination of Gold (I& III) in Water Using the Ion - Pairing Amiloride Hydrochloride

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Abstract

The chemical equilibrium of the ternary complex ion associate of the complex anion AuCl_4^- and the ion – pairing reagent 1- (3, 5-diamino-6-chloropyrazinecarboxyl) guanidine hydrochloride monohydrate, DPG^+Cl^- extracted from aqueous solutions of pH 5-6 onto 4-methyl pentan-2-one was demonstrated. The extraction constants (K_{ex} , K_D and B) of the chemical equilibrium and the structure of the produced associate were determined. The results have indicated that, the formation of the complex ion associate of the chemical structure $\text{DPG}^+\text{AuCl}_4^-$ and the extraction mechanism does not involve solvation of the ion associate by the amine and/or water molecules in the organic phase. Beer's law was obeyed in the range 0.01 -2.5 $\mu\text{g mL}^{-1}$ gold (III) in the aqueous solution. The method was applied successfully for the analysis of gold (I) after oxidation to gold (III). The method was also applied for the analysis of gold (I& III) at trace concentrations in industrial wastewater samples. Gold (III) ions at trace level in one liter aqueous solution was concentrated in 10.0 mL by the developed extraction system so an enrichment factor of 100 was achieved. The time taken for the separation and determination of gold ions was in the range of 3-5 min.

Keywords: Chemical equilibria, Speciation of gold (I, III), Ion associate, Wastewater

1. Introduction

Gold is one of the most important noble metals due to its wide application in industry and economic activity. Gold occur on the Earth in very low natural contents and its concentration in natural water is extremely low, in the range of 0.05 - 0.2 ng mL^{-1} . It is well known that gold is one of the most interesting micro amount elements due to its significant role on biology and environment. Thus, simple, sensitive and selective methods for determination of trace gold are of great importance.

Several sophisticated techniques, such as laser induced breakdown spectroscopy, inductively coupled plasma mass spectrometry (ICP –MS), inductively coupled plasma atomic emission spectrometry (ICP-AES), electrochemical, neutron activation analysis, total reflection X-ray fluorescence spectrometry have been applied to the determination of gold (Shourshein, 2010, PP. 89 -95; Guanghan, 1992, PP. 51-53; Medved, 2004, PP. 60 – 65; Yu, 2003, PP. 225 -231; Navratilova, 2000, PP. 369-372; Itagaki, 2000, PP. 344-349 and Li, 2006, PP. 841-844) in various matrices including wastewater. However, some of these methods are less often applied in gold analysis due to the complexity and cost of the required instrumentation (Guanghan, 1992, PP. 51-53; Medved, 2004, PP. 60 – 65; Yu, 2003, PP. 225 -231; Navratilova, 2000, PP. 369-372). Thus, spectrophotometric methods still have the advantages in respect of simplicity and low operating costs.

Recently (Zuotao, 1999, PP. 237-241; Pyrzynska, 2005, PP. 1316-1322; Hu, 2006, PP. 627-630 and Fazli, 2009, PP. 210-212) a wide variety of spectrophotometric methods for the determination of gold have been reported. The ion pairing reagents had widely been applied for the pre concentration and/or determination of noble metal ions (Filatova, 2004, PP. 243-245; El-Shahawi, 2005, PP. 319-326; Hassan, 2005, PP.673- 678; El-Shahawi, 2008, PP.313 - 319). Charged bulky cations e.g. amidine, rhodamine derivatives, basic dyes, 18- crown-6 (18C6) oxonium cation, tetra alkyl ammonium, phosphonium or arsonium halides and tetrazolium salts are often used to form extractable complex ion associates with charged bulky oxoanions or anionic complex species of gold (I) , gold (III) and other metal ions as their halides, cyanides and thiocyanates (Haddad, 1988, PP. 23 – 36; Burns, 1992, PP. 213-215; Burns, 1992, PP. 131-132; El-Shahawi, 1996, PP. 2037-2043; Biswas, 1996, PP. 804-80; Camagong, 2001, PP. 1725-1728; Farag, 2007, PP. 218-228 and Bashammakh, 2009, PP. 413 – 418). Burns, 1988, PP. 185-187 and Burns, 1996, PP.107-109 and other workers (El-Shahawi, 1997, PP. 85-91; AlDhaheri, 1998, PP. 161-1615 and El-Shahawi, 2007, PP.1494-1499) have used the reagent amiloride mono hydrochloride

extensively as a selective ion-pairing reagent for the determination of some oxoanions e.g. perchlorate, perrhenate, periodate and tetra chloroaurate (AuCl_4^-) in different matrices.

Recent literature survey on the title ion – pairing reagent has revealed no study on the chemical equilibrium of the reagent DPG^+Cl^- with AuCl_4^- . Hence, the main objectives of the present article was focused on:

- i. Studying the chemical equilibrium of the reagent DPG^+Cl^- with AuCl_4^- in an attempt to develop a precise extractive spectrophotometric method for the determination and chemical speciation of gold (I, III) species in wastewater samples.
- ii. achieving a better association and a better understanding of the extraction mechanism of the produced ion associate of DPG^+Cl^- with AuCl_4^- in the organic phase.

2. Experimental

2.1 Chemicals and reagents

Analytical reagent grade chemicals and solvents (BDH, Poole, UK) were used as received. Potassium aurate [KAuCl_4] and potassium aurocyanide, [$\text{KAu}(\text{CN})_2$] (Fluka AG, USA) were used for the preparation of stock solutions of gold (III) and gold (I) ions, respectively. The reagent, DPG^+Cl^- (Merck, India) was used without purification. A stock solution (0.01 mol L^{-1} , 100 mL) of the reagent DPG^+Cl^- was prepared by dissolving an accurate weight (0.302g) of it in $\text{H}_2\text{O}-\text{HCl}$ (1:1 v/v). Britton - Robinson (B-R) buffer of pH 2.1 - 11 was prepared (Vogel, 1966).

2.2 Apparatus

A double beam Perkin-Elmer (model Lambda EZ-210, USA) spectrophotometer (190-1100 nm) with 1 cm (path width) quartz cell was used for recording the electronic spectra and the absorbance of the organic extracts. Infrared (IR) spectra were recorded on a Brucker FT-IR (model IFS 66, USA) spectrophotometer. A Perkin-Elmer (Analyst TM 800, USA) flame atomic absorption spectrometer (FAAS) was used for measuring the concentration of gold ions at 242.8 nm at 0.5 nm slit width before and after extraction with the organic solvent. De - ionized water was obtained from Milli-Q Plus system (Millipore, Bedford, MA, USA) and the pH were recorded on a pH meter (Orion EA940, MA, USA) with absolute accuracy limits being defined by NIST.

2.3 Recommended extraction procedures

2.3.1 Determination of the extraction equilibrium constants (K_D , β , K_{ex})

Aliquot aqueous solutions of gold (III) ions (10 mL , $1-10 \mu\text{g mL}^{-1}$) at pH 5-6 were transferred to separating funnels (50.0 mL). A 2 mL of the reagent DPG^+Cl^- solution ($8.0 \times 10^{-5} \text{ mol L}^{-1}$) was added to each gold solution. The solutions were completed with B-R buffer of pH 5-6 to the mark of measuring flasks (25 mL). Each reaction mixture was mixed well and extracted twice ($2 \times 2.5 \text{ mL}$) with 4-methyl pentan-2-one for 2 min. The two phases were then separated out and the organic extract was collected in a 25 mL beakers containing anhydrous Na_2SO_4 (1.0g). The contents were swirled to mix and transferred to volumetric flask (10 mL). The solid residue was then washed with another 5 mL ($2 \times 2.5 \text{ mL}$) of the solvent and the washings were transferred to the measuring flask. The flask was made up to the mark with the solvent. The absorbance of the organic extract was then measured at 362 nm against blank. The extraction procedures were also carried out in separate experiments at pH 5-6 of the aqueous solutions. After extraction, the gold (III) remained in the aqueous phase (C_a) was determined with FAAS. The amount of gold ions of the parallel aqueous solution containing the same amount of gold (III) ions before (C_b) extraction was also measured by FAAS. The amount of gold (III) ions extracted in the organic phase was finally calculated by difference ($C_b - C_a$) between the amount of gold (III) ions before and after extraction. The distribution ratio (D_{Au}) of the extraction step was calculated as reported (Burns, 1996, PP. 107-109 and El-Shahawi, 1997, PP. 85-91). Following these procedures, the effect of the diverse ions on the accuracy of the developed method for gold (III) was investigated.

2.3.2 Determination of gold (I)

An aliquot portion (10 mL) of the aqueous solutions containing gold (I) at concentration $< 5 \mu\text{g mL}^{-1}$ was transferred to conical flask (50 mL) and oxidized to gold (III) with bromine water after boiling for 5 min in a closed system (to avoid the evaporation of gold species) and finally cooled to room temperature ($25 \pm 1^\circ\text{C}$). The gold (III) produced was adjusted to pH 5-6 and completed to the mark with B-R buffer of pH 5-6. The resulting solution was then analyzed following the recommended procedures for gold (III) determination at 365 nm versus the reagent blank with the aid of standard curve.

2.4 Analytical application

Industrial wastewater samples (100 mL) of fertilizer industry from the boundary side of Jeddah city , Saudi Arabia were collected and filtered through a 0.45 μm membrane filter. The solution pH was then adjusted to pH 5-6 with Britton – Robinson buffer and an accurate amount (0.5 - 10.0 μg) of gold (III) species was added. To the test solution an accurate amount of the reagent DPG⁺.Cl⁻ (2.0 mL, 8.0×10^{-5} mol L⁻¹) was added to the sample solution and the solution mixture was then transferred to 100 mL separating funnel. The organic extract was separated out and the absorbance was measured at 362 nm against reagent blank. The concentration of gold (III) in the organic and aqueous phases was also determined with FAAS.

3. Results and discussion

3.1 Extraction equilibrium

On mixing the complex anion AuCl₄⁻ with the reagent DPG⁺.Cl⁻ in aqueous solutions of pH 5-6 containing sodium chloride (10 % m/v) and shaking with the solvent 4-methyl pentan-2-one for about 2 min, a yellow colored complex ion associate was developed in the organic phase. The electronic spectrum of the organic extract in 4-methyl pentan-2-one showed one well defined peak maximum at 362 nm. Thus, the absorbance of the organic extract of AuCl₄⁻ and DPG⁺.Cl⁻ was measured at 362 nm against reagent blank. Assuming no dimerization of the extracted species, the formation of polynuclear complex species is negligible (Alexandrov, 1997, PP. 26-32) and the complex anion AuCl₄⁻_(aq) is only predominant at the given pH, the overall reaction between the reagent DPG⁺.Cl⁻_(aq) and HAuCl₄_(aq) is most likely proceeded as follows (Kamburova, 1992, PP. 997 -1001 and Hiraoka, 1982, PP. 243-245) :

I. Formation of a ternary complex ion associate in the aqueous phase as follows:



The corresponding equilibrium constant, β is given by the equation:

$$\beta = [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{org})} / [\text{AuCl}_4^-]_{(\text{aq})} [\text{DPG}^+]_{(\text{aq})} \quad (2)$$

II. Distribution of the complex ion associate between the aqueous and organic phases:



with a distribution constant, K_D which is given by the equation:

$$K_D = [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{org})} / [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{aq})} \quad (4)$$

III. Extraction of the complex anion AuCl₄⁻ as follows:



The corresponding extraction constant, K_{ex} is then given by the equation:

$$K_{\text{ex}} = [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{org})} / [\text{DPG}^+]_{(\text{aq})} [\text{AuCl}_4^-]_{(\text{aq})} = K_D \beta \quad (6)$$

Assuming the complex species AuCl₄⁻_(aq) is the only predominant species in the aqueous phase at equilibrium at the given pH, the value of the distribution ratio, D_{Au} was then determined at constant concentration of AuCl₄⁻ and various amounts of the reagent DPG⁺.Cl⁻ in the aqueous phase employing the equation (Kamburova, 1992, PP. 997 -1001 and Alexandrov, 1997, PP. 26-32):

$$D_{\text{Au}} = [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{org})} / [\text{AuCl}_4^-]_{(\text{aq})} + [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{aq})} \quad (7)$$

At low DPG⁺.Cl⁻_(aq) concentration, the term $[\text{DPG}^+\text{.AuCl}_4^-]_{(\text{aq})}$ can be neglected and equation (7) takes the form:

$$D_{\text{Au}} = [\text{DPG}^+\text{.AuCl}_4^-]_{(\text{org})} / [\text{AuCl}_4^-]_{(\text{aq})} \quad (8)$$

Substituting equation (8) into equations (2) and (6) and taking the logarithms, equation (9) is obtained:

$$\log D_{\text{Au}} = \log K_D + \log \beta + \log [\text{DPG}^+\text{.Cl}^-] \quad (9)$$

The values of D_{Au} at the initial concentration of AuCl₄⁻ (1×10^{-6} mol L⁻¹) in the aqueous phase (pH5-6) at various concentrations ($1.0 - 40.0 \times 10^{-5}$ M) of the reagent DPG⁺.Cl⁻ were then calculated. The plot of $\log D_{\text{Au}}$ versus $\log [\text{DPG}^+\text{.Cl}^-]$ was linear (Figure 1) with a slope of 0.91 confirming the formation of 1:1 molar ratio of DPG⁺ and

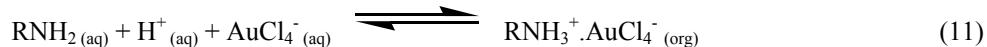
AuCl_4^- in the formation of ternary complex ion associate $\text{DPG}^+ \cdot \text{AuCl}_4^-$. The data also have the existence of AuCl_4^- species in the organic solvent and the absence of non-specific interaction between the ion associate and the reagent $\text{DPG}^+ \cdot \text{Cl}^-$ and also between the bulky anion $[\text{AuCl}_4]_{(\text{aq})}$ and the organic solvent (Hiraoka, 1982, PP.243-245; Alguacil, 1996, PP. 197-208 and El-Shahawi, 1997 PP85 -91). At high concentration of the reagent $\text{DPG}^+ \cdot \text{Cl}^-$, the respective term $[\text{AuCl}_4]_{(\text{aq})}$ is negligible and equation (7) takes the following form:

$$D_{\text{Au}} = [\text{DPG}^+ \cdot \text{AuCl}_4^-]_{(\text{org})} / [\text{DPG}^+ \cdot \text{AuCl}_4^-]_{(\text{aq})} = K_D \quad (10)$$

Thus, at high $\text{DPG}^+ \cdot \text{Cl}^-$ concentration, the plot of the experimental data in the same coordinates of equation (9) has yielded a straight line slightly parallel to the abscissa with negative slope of -0.04 close to zero (Figure 1) confirming, the proposed chemical model, the proposed ternary complex ion associate, the absence of non-specific interaction between the produced complex associate and the reagent and also between the bulky anion $[\text{AuCl}_4]_{(\text{aq})}$ and the organic solvent (Hiraoka, 1982, PP. 243-245 and Alguacil, 1996, PP.197-208). The data have also confirmed the non-specific interaction between the extracted species $\text{DPG}^+ \cdot \text{AuCl}_4^-$ and the solvent (Hiraoka, 1982, PP. 243-245 and Alguacil, 1996, PP.197-208). The values of the equilibrium constants (β and K_D) and the extraction constant, ($K_{\text{ex}} = \beta \times K_D$) of the formed ion associate computed from the linear plot (Figure 1) are: $\beta = 2.07 \pm 0.2 \times 10^4$, $K_D = 11.97 \pm 0.7$, $K_{\text{ex}} = 2.0 \pm 0.3 \times 10^3$. Using these constants, the theoretical correlation of D_{Au} as a function of $\text{DPG}^+ \cdot \text{Cl}^-$ was calculated. The results revealed satisfactory agreement between the experimental and the theoretical data confirming the molar ratio (1:1) of the reagent $\text{DPG}^+ \cdot \text{Cl}^-$ to the complex anion AuCl_4^- in the extracted complex ion associate $\text{DPG}^+ \cdot \text{AuCl}_4^-$. The computed values of the extraction constants β , K_D and K_{ex} are better than the data reported (Patel, 1986,PP. 1547 -1551) using amidine ion pair. The developed extraction procedures also offered lower reaction time, much less toxic option and low cost for the separation and/or determination of gold (III) species.

3.2 Extraction mechanism

Assuming an overall gold (III) extraction in which the reagent amiloride abbreviated by RNH_2 has the general equilibrium equation:



$$K_{\text{ex}} = [\text{RNH}_3^+ \cdot \text{AuCl}_4^-]_{(\text{org})} / [\text{AuCl}_4^-]_{(\text{aq})} [\text{H}^+]_{(\text{aq})} [\text{RNH}_2]_{(\text{aq})} \quad (12)$$

On substituting equation (1) onto equation (10) equation (13) was obtained:

$$K_{\text{ex}} = D_{\text{Au}} / [\text{H}^+]_{(\text{aq})} [\text{RNH}_2]_{(\text{aq})} \quad (13)$$

Taking logarithms and rearranging the equation, the following equation :

$$\log D_{\text{Au}} = \log K_{\text{ext}} - \text{pH} + \log [\text{RNH}_2]_{(\text{aq})} \quad (14)$$

was obtained and the corresponding coefficients for the pH and the amiloride concentration was achieved. The plot of pH versus $\log D_{\text{Au}}$ at constant reagent concentration and the aqueous phase containing 0.25 mmol L^{-1} gold (III) using aqueous/organic phase volume ratio of 1/1 and shaking for 3 min was linear with a slope 0.965 close to unity confirming the value for the pH coefficient given in equation (14). Based on the work reported earlier (Alguacil, 1996, PP. 197-208) and by definition, when $D_{\text{Au}} = 1$ in a solvent extraction system, the pH obtained is known as pH_{50} . Thus, on replacing pH_{50} in equation (11), the following expression was obtained:

$$\text{pH}_{50} = \log K_{\text{ext}} + \log [\text{RNH}_2]_{(\text{aq})} \quad (15)$$

On plotting $\log D_{\text{Au}}$ versus $\log [\text{RNH}_2]_{(\text{aq})}$ (Figure 1) a slope of 0.956 was obtained. This value close to unity and corresponds to the value of $\log [\text{RNH}_2]$ coefficient given in equations (13) and (14). Elemental analysis of the produced ternary complex ion associate in the solid form after solvent evaporation: $[\text{AuOC}_6\text{H}_9\text{N}_7\text{Cl}_5]$ required: 12.6% C, 1.57% H, 17.2% N, 31.1% Cl and 34.7% Au; Found 12.9% C, 1.7% H, 17.7% N, 31.7 % Cl and 35.6 % Au. The IR spectra of the reagent $\text{DPG}^+ \cdot \text{Cl}^-$ and its solid ion complex associate recorded in KBr disk showed the characteristic frequencies of ν (N-H), ν (N-N), ν (N-H) +(C-N), ν (N-C-S) and ν (Au-Cl) vibrations at 3456 (br.), 1626 (s), 1516 (s) and 450 cm^{-1} (Nakamoto, 1978, PP. 232 -239), respectively confirming the proposed structure. The results also added further conclusive evidence that, the amiloride reagent extracted gold (III) from the aqueous solution containing $[\text{AuCl}_4]_{(\text{aq})}$, and the absence of non-specific interaction between the ion associate and the reagent $\text{DPG}^+ \cdot \text{Cl}^-$ and also between the bulky anion $[\text{AuCl}_4]_{(\text{aq})}$ and the organic solvent (Hiraoka, 1982, PP.243-245 and Alguacil, 1996, PP. 197-208). Thus, the extraction mechanism of the anion AuCl_4^- from the aqueous solution at pH 5- 6 by the reagent $\text{DPG}^+ \cdot \text{Cl}^-$ did not involve solvation of the produced ion associate ($\text{DPG}^+ \cdot \text{AuCl}_4^-$) in the organic phase by amine and/or water molecules (Hiraoka, 1982,

PP.243-245 and Alguacil, 1996, PP. 197-208).

3.3 Analytical performance

The plot of the absorbance of the developed ion associate $\text{DPG}^+\text{AuCl}_4^-$ (org) in the organic phase at 362 nm vs. gold (III) concentration (C , $\mu\text{g mL}^{-1}$) was linear confirming Beer's-Lambert law (Marczenko, 1986, PP. 68 – 70 and Miller, 1994, PP.115-125) in the concentration range 0.01 -2.5 $\mu\text{g mL}^{-1}$ gold (III) in the aqueous solution with a correlation coefficient of 0.99. The molar absorptivity calculated from Beer's-Lambert plot and the Sandell's sensitivity index (Marczenko, 1986, PP. 69 -70) of the ion associate were found $2.05 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, $0.069 \mu\text{g cm}^{-2}$, respectively. The effective concentration range of gold (III) as evaluated by Ringbom's plot (Marczenko, 1986, PP. 69 -70) was found equal $1.5\text{-}1.5 \mu\text{g mL}^{-1}$. A lower limit of detection (LOD) of $0.005 \mu\text{g mL}^{-1}$ was achieved using of the formula $\text{LOD} = 3S_{y/x}/b$ where, $S_{y/x}$ is the standard deviation of y - residual and b is the slope of the calibration plot (Miller, 1994, PP.115-125). The lower limit of quantification (LOQ = $10S_{y/x}/b$) under the established conditions for gold (III) was $0.033 \mu\text{g mL}^{-1}$. The LOD could be improved to lower value by increasing the sample volume of the aqueous phase containing ultra trace concentration of gold and amiloride at the optimum experimental conditions and shaking with the organic solvent. A relative standard deviation (RSD) of 2.96 % (n=5) was obtained for gold (III) at concentration $0.5 \mu\text{g mL}^{-1}$. The figure of merits (LOD, linear range, RSD) of the proposed procedure was compared with many of the reported spectrometric methods and in the literature (Pyrzynska, 2005, PP. 1316-1322; Fazli, 2009, PP. 210-212; Zuotao, 1999, PP. 237-241 and El-Shahawi, 2008, PP. 313 -319). The time consuming on the developed method is comparable with some reported methods (Pyrzynska, 2005, PP. 1316-1322 and Fazli, 2009, PP. 210-212) confirming its precision.

3.4 Interference studies

The selectivity of the developed method for the determination of gold (III) at $1.0 \mu\text{g mL}^{-1}$ was tested in the presence of a relatively high excess ($0.1\text{-}1 \text{ mg mL}^{-1}$) of some diverse ions which are often accompanying gold in water. The tolerance limit was defined as the concentration of the diverse ion added causing a relative error in the absorbance at 362 nm in the range $\pm 3\%$. A recovery percentage of $100 \pm 2.5\%$ gold (III) and a standard deviation of ± 0.12 were achieved in the presence of the ions: Li^+ , Na^+ , K^+ , Ca^{2+} , NH_4^+ , Al^{3+} , Fe^{2+} , Fe^{3+} , Ni^{2+} , Co^{2+} , Pd^{2+} , Pt^{2+} , Cu^{2+} , Zn^{2+} and Ag^+ at 1:100 tolerable concentration of gold(III) to the diverse ions, respectively. The ions Fe^{3+} , MnO_4^- , VO_3^- and NO_3^- interfered seriously even at low concentrations. The positive interference of these ions is most likely assigned to the ability of these anions to form relatively stable complex ion associates with the reagent DPG^+Cl^- . Interference of MnO_4^- was eliminated by adding traces of NaN_3 (0.1%w/v) while, the influence of the ions Fe^{3+} and VO_3^- was minimized successfully by the addition of NaF (0.1%) and promotes unambiguous and sensitive determination of gold (III).

3.5 Analytical applications

3.5.1 Analysis of gold (I) and / or gold (III)

The values of the extraction constants (K_D , β and K_{ex}) in the present study and the molar absorptivity suggested the application of the developed extraction equilibria for extractive spectrophotometric determination of gold (III) at trace concentrations of gold ($0.05 - 2.0 \mu\text{g mL}^{-1}$). Different amounts of gold (III) were spiked onto distilled water (100.0 mL) and the solutions were subjected to the pre recommended extraction procedures. A satisfactory recovery percentage in the range $96\text{-}98 \pm 3\%$ was obtained between the amount of gold (III) added and measured confirming the accuracy of the developed procedures. The developed procedure was also applied successfully for the determination of gold (I) species at various concentrations ($0.1\text{-}2.0 \mu\text{g mL}^{-1}$) after oxidation to gold (III) with Br_2 water in the presence of HCl as described earlier (El-Shahawi, 2007, PP.1494-1499). A recovery percentage ($98 \pm 3.4\%$, $n = 5$) of gold (I) was also achieved suggesting the use of the method for the analysis of total inorganic gold and chemical speciation of gold (I & III) species and in aqueous media. Thus, the analysis of the binary mixture of gold (I) and (III) at a total amount ($10\text{-}20 \mu\text{g}/25 \text{ mL}$ aqueous solution) was carried out as follows: an aliquot mixture was first determined according to the described procedure for gold (III). Another aliquot mixture was oxidized to gold (III) with bromine water-HCl (El-Shahawi, 2007, PP.1494-1499) and determined as described in for gold (I) species. Gold (I) ions in the water samples were then determined by the difference ($A_2 - A_1$) between the absorbance of the aliquots before (A_1) and after (A_2) oxidation. The results are summarized in Table 1. A satisfactory recovery percentage in the range 96.6-103.2% was obtained with good reproducibility. A relative standard deviation in the range of 1.9-2.3 and 2.1-2.2% for gold (I) and (III) was also obtained, respectively. The proposed method was compared favorably with FAAS and the dithizone spectrophotometric methods i(Marczenko, 1986, P. 303) for gold (III) determination. The value of the Student's t - test ($t = 2.61$ at 95%) was found greater than the theoretical one ($t = 2.31$), so there is no significance differences between the two means.

3.5.2 Analysis of gold in wastewater

The extraction procedure was also applied for the separation and subsequent determination of gold (III) by the standard addition of gold (III) species at 5-10 $\mu\text{g mL}^{-1}$ onto industrial wastewater samples. A 100.0 mL of water samples was filtered, adjusted to the required pH and extracted as described in the experimental section. The organic extract was analyzed for gold by the developed extractive spectrophotometric method and also by the standard FAAS. The results are given in Table 2. An acceptable recovery percentage of gold (III) in the range of $98\text{-}103 \pm 2.42\text{-}3.2\%$ was achieved. The decrease in the recovery percentage at 5.0 $\mu\text{g mL}^{-1}$ gold was improved by increasing the shaking time of the aqueous test solution with the ion pair reagent to 3 -4 min. The t- and F-tests at 95% confidence levels did not exceed the tabulated (theoretical) ones and revealed no significant differences (Table 2) between the averages and the variances of the developed and the standard FAAS methods. At 95% confidence, the calculated value of $t = 2.43$ is greater than the theoretical one ($t=2.31$) so there is a difference between the two means.

4. Conclusion

The reaction of the reagent DPG^+Cl^- with AuCl_4^- is rapid (the time taken for the separation and determination of gold ions is at most 3-5 min) and does not involve any stringent conditions. The values of K_D , β , and K_{ex} , of the produced associate $\text{DPG}^+\text{AuCl}_4^-$ compete favorably with the most ion pair reagents (El-Shahawi, 1996, PP. 2037-2043 and Patel, 1986 and PP. 1547.-1551) and allowed the use of the system for photometric determination of gold (III). Gold (III) ions at trace or ultra trace in one liter aqueous solution was concentrated in 10.0 mL by the developed system so an enrichment factor of 100 was achieved. The extraction system is also suitable for the chemical speciation of gold (I, III) ions.

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Table 1. Analytical data of gold (I) and gold (III) in their binary mixtures in aqueous media (10 mL) by the proposed extractive spectrophotometric method

Gold species,				Recovery, %*	
Taken, µg		Found, µg			
Au ⁺	Au ³⁺	Au ⁺	Au ³⁺	Au ⁺	Au ³⁺
5.0	5.0	4.8	5.1	96.0±2.3	102.0±2.3
10.0	10.0	9.75	10.22	97.5±2.9	102.4 ±2.1
10.0	10.0	9.80	9.90	99.4±2.7	99.0±1.9

* Average (n=5) ± relative standard deviation.

Table 2. Results of the extractive spectrophotometric determination of gold (III) spiked (0.5 – 10 µg) to industrial wastewater samples (100 mL)

Gold species,		Recovery, %*
Gold (III) added, µg	Gold (III) found, µg	
0.0	0.0	0.0
5.0,	4.9± 0.12	98.± 2.42.
8.0	8.2± 0.22	5.0± 2.7
10.0	10.3± 0.32	103.0±3.2

*Average (n=5) ± relative standard deviation.

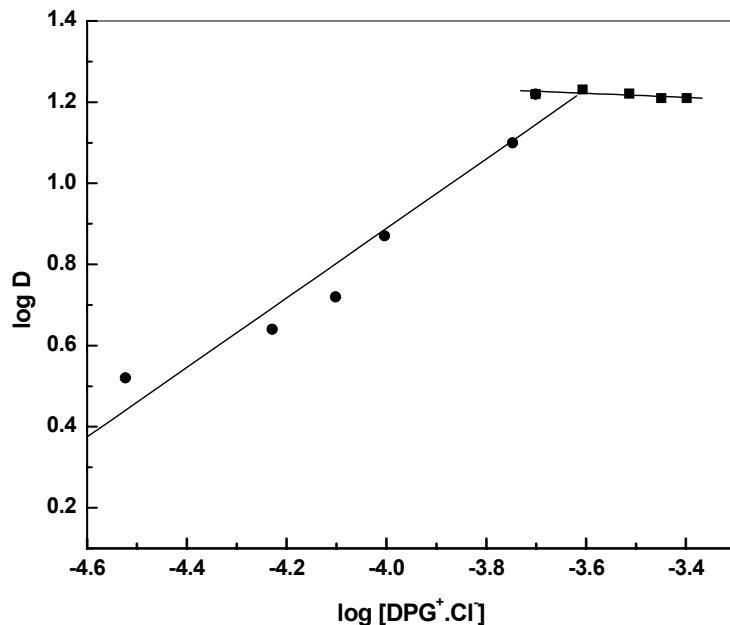


Figure 1. Plot of $\log [DPG^+\cdot Cl^-]$ versus $\log D_{Au}$ of the ion associate $[DPG^+\cdot AuCl_4^-]$ Conditions: Aqueous phase (20 mL) at pH 6-7, organic solvent = 5 mL and $[HAuCl_4] = 6.2 \times 10^{-6} \text{ mol L}^{-1}$