

Chemical speciation and recovery of gold(I, III) from wastewater and silver by liquid–liquid extraction with the ion-pair reagent amiloride mono hydrochloride and AAS determination

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Abstract

A novel and low cost liquid–liquid extraction procedure for the separation of gold(III) at trace level from aqueous medium of pH 5–9 has been developed. The method has been based upon the formation of a yellow colored ternary complex ion associate of tetrachloro gold(III) complex anion, AuCl_4^- with the ion-pair reagent 1-(3,5-diamino-6-chloropyrazinecarboxyl) guanidine hydrochloride monohydrate, namely amiloride, $\text{DPG}^+\cdot\text{Cl}^-$. The effect of various parameters, e.g. pH, organic solvent, shaking time, etc. on the preconcentration of gold(III) from the aqueous media by the $\text{DPG}^+\cdot\text{Cl}^-$ reagent has been investigated. The colored gold species was quantitatively extracted into 4-methyl pentan-2-one. The chemical composition of the ion associate of $\text{DPG}^+\cdot\text{Cl}^-$ with AuCl_4^- in the organic solvent has been determined by the Job's method. The molar absorptivity ($2.19 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) of the associate $\text{DPG}^+\cdot\text{AuCl}_4^-$ at 362 nm enabled a convenient application of the developed extraction procedure for the separation and AAS determination of traces of aurate ions. Mono-valence gold ions after oxidation to gold(III) with bromine water in HCl (1.0 mol L^{-1}) media have been also extracted quantitatively from the aqueous media by the developed procedure. The chemical speciation of mono- and/or tri-valence gold species spiked to fresh and industrial wastewater samples has been achieved. The method has been also applied successfully from the separation of gold(I) and gold(III) species from metallic ions and silver. The developed method has also the advantage of freedom from most diverse ions.

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1. Introduction

Gold is widely distributed in nature and the chemistry of gold remains an active research area [1]. Some gold(I) compounds are biologically active and used as anti-inflammatory drugs in the treatment of rheumatoid arthritis [1–3]. Due to the low level of gold in the environmental samples and its great importance, many articles have been reported on the separation of traces of gold in water and other matrices containing Cd^{2+} , Zn^{2+} , Cu^{2+} , Ni^{2+} , Mn^{2+} , Co^{2+} , Pd^{2+} , Hg^{2+} , Pb^{2+} , Pt^{4+} , Fe^{3+} , alkaline and alkaline earth ions before their actual determination [3–9]. The spectrometric methods, e.g. ICP-AES, FAAS, ETAAS, electrophoresis and other spectrophotometric methods involving 2-carboxyl-1-naphthalthiorhodanine (CNTR), Spheron (R) and

(biphenyl) dimethanethiol, etc. are the most used techniques in the analysis of gold at low level [7,9–15]. Few of these methods have sufficient sensitivity and selectivity for the trace levels of mono- and tri-valence gold species in fresh water and industrial wastewater samples [7,11–15]. However, the low level of gold in drinking waters is not compatible with the detection limit and some of these methods are expensive, unselective and require careful experimental conditions and considerable time consuming. Thus, preconcentration and separation techniques using liquid–liquid and liquid–solid are frequently required to improve the detection capability and the selectivity of these techniques [7,12–14].

The ion-pair reagents containing bulky anions are often used to form extractable complex ion associates with charged bulky cationic complex species of neutral ligands, e.g. crown ethers, *o*-phenanthroline derivatives, and metal ions [6–10,16–18]. On the other hand, the bulky cations, e.g. rhodamine derivatives, basic dyes, 18-crown-6 (18C6) oxonium cation, tetra alkyl

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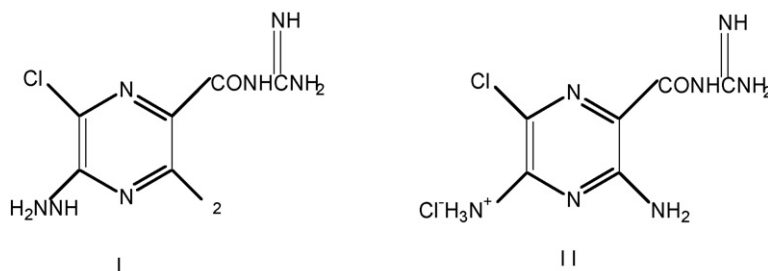


Fig. 1. Chemical structures of the amiloride (I) and amiloride hydrochloride (II).

phosphonium or arsonium halides and tetrazolium salts are also often used to form extractable ion associates with charged bulky oxoanions or bulky anionic complexes of metal [18–30] and gold(III) halides, cyanide and thiocyanate [31–33].

Burns et al. [34,35] and others [36,37] have been successfully used the compound amiloride mono hydrochloride (Fig. 1) as a selective analytical ion-pair reagent for the determination of the oxoanions perchlorate, perrhenate and periodate in different matrixes. The extraction of the produced complex ion associates of amiloride with these oxoanions proceeded rapidly with high recovery factor [27–31].

Recent years [7,10–15] have seen an upsurge of interest for rapid and sensitive analytical methods for the separation and speciation of chemical forms of precious metal ions in environmental samples. A recent literature on the analytical applications of the ion-pair reagent $\text{DPG}^+\cdot\text{Cl}^-$ has revealed no study on the use of the reagent on the liquid–liquid separation of gold(III) from silver and other base metal ions and chemical speciation of chemical forms of mono- and tri-valent gold ions. Thus, the goals of the present article are focused on the use of the title reagent for the separation of gold(III) and speciation of chemical forms of mono- and tri-valence gold species as a ternary complex ion associate of AuCl_4^- and $\text{DPG}^+\cdot\text{Cl}^-$ in non-aqueous media. The extraction mechanism and the chemical separation of gold(I) and (III) species from silver(I) and other base metal (Fe^{3+} , Co^{2+} , Ni^{2+} , and Cu^{2+}) ions have been also included.

2. Experimental

2.1. Reagents and materials

Analytical reagent grade chemicals nickel(II) sulphate, iron(III) sulphate and copper(II) sulphate and solvents (BDH, USA) were used. Potassium aurocyanide, $\text{KAu}(\text{CN})_2$ (Fluka AG, USA), chloroauric acid, HAuCl_4 (Johnson Mathey & Co., UK), silver nitrate (Fluka, USA) and amiloride mono hydrochloride (E Merck, India) were used for the preparation of stock solutions ($1000\ \mu\text{g mL}^{-1}$) of gold(I), gold(III) and silver(I) ions, respectively. A stock solution ($0.01\ \text{mol L}^{-1}$) of amiloride mono hydrochloride (E Merck, India) was prepared by dissolving an accurate weight (0.03 g) of the reagent in 100 mL $\text{H}_2\text{O}-\text{HCl}$ (1:1, v/v). Double distilled de-ionized water was used throughout the work for the preparation of stock solutions ($1000\ \mu\text{g mL}^{-1}$). A series of Britton–Robinson buffers ($0.04\ \text{mol L}^{-1}$ in each of acetic, orthophosphoric, and boric acids) adjusted to the

required pH with sodium hydroxide ($0.2\ \text{mol L}^{-1}$) was prepared [38].

2.2. Apparatus

Carbon, hydrogen and nitrogen content were determined on a Perkin-Elmer 2400C series elemental analyzer, USA. A Perkin-Elmer (model Lambda EZ-210, USA) spectrophotometer (190–1100 nm) with a 10 mm long quartz cell was used for recording the electronic spectra of the reagent and the complex ion associate of gold(III). The absorbance of the organic extract was measured with a single beam Perkin-Elmer (model Lambda EZ-150, USA) UV–vis spectrophotometer with quartz cell (10 mm). A Perkin-Elmer (Analyst TM 800, USA) furnace atomic absorption spectrometer (AAS) was used for measuring the concentration of Au, Ag, Fe, Ni, and Cu at the wavelengths 242.8, 328.1, 372.0, 232.0 and 324.7 nm, respectively at 0.5 nm slit width except for iron and nickel at 0.2 nm before and after separation step from the aqueous phase under instrument's optimum settings.

2.3. Recommended extraction procedures

2.3.1. Extraction procedures of gold(III) species

In a separating funnel (50 mL), a 2 mL aliquot of the ion-pairing reagent $\text{DPG}^+\cdot\text{Cl}^-$ ($1.0 \times 10^{-5}\ \text{mol L}^{-1}$) was mixed with 9.0 mL of B–R buffer (pH 6–7) containing various concentrations ($(1.0-6) \times 10^{-5}\ \text{mol L}^{-1}$) of HAuCl_4 to adjust the pH of the final aqueous solution. The aqueous solution was then diluted to 20.0 mL with double distilled water. The aqueous solution was shaken twice, each with 2.5 mL of the solvent 4-methyl pentan-2-one for 2 min. After separation of the layers, the organic extract was then collected in a 25 mL beaker containing anhydrous sodium sulphate (1.0 g) swirled to mix the contents and transferred to a 10 mL volumetric flask. The residue was also washed with 5 mL (2×2.5) of the same organic solvent, transferred to the measuring flask and finally made up to the mark with the same solvent. The absorbance of the organic extract was then measured at 362 nm against a reagent blank. After extraction, the pH of the aqueous phase was determined as equilibrated pH and the amount of gold ions remained in the aqueous phase (C_f) was determined also by AAS. The amount of gold ions of the parallel samples containing the same amount (C_i) of gold(III) ions and the reagent $\text{DPG}^+\cdot\text{Cl}^-$ was also measured by AAS. The amount of gold(III) ions in the organic phase was finally calculated by

the difference ($C_i - C_f$) and the distribution ratio (D_{Au}) was then calculated employing the equation:

$$D_{Au} = \frac{[DPG^+ \cdot AuCl_4^-]_{(org)}}{[AuCl_4^-]_{(aq)} + [DPG^+ \cdot AuCl_4^-]_{(aq)}} \quad (1)$$

2.3.2. Extraction procedures of gold(I) species

An accurate volume (10 mL) of the aqueous solution containing gold(I) ions at different concentrations ($1.0\text{--}15 \mu\text{g mL}^{-1}$) was transferred to the conical flask (50 mL capacity). Another 10 mL of HCl (1 mol L^{-1}) and bromine water (2 mL) were added to oxidize gold(I) solutions to gold(III) complex species. The solutions were left for 5 min and the excess Br_2 and HCl were then removed by boiling the solutions for 10–15 min and finally allowed to cool to room temperature ($25 \pm 1^\circ\text{C}$). The solution mixtures were then adjusted to pH 6–7 with B–R buffer, transferred with the washing solutions to a 50 mL separating funnels. The resulting solutions were then extracted as described earlier for gold(III) extraction. The concentration of the produced gold ions was then determined with AAS using calibration curves of gold(III) and (I) ions.

2.3.3. Extraction of the binary mixtures of gold(I) and (III)

An aliquot (10 mL) of a mixture of mono- and tri-valent gold ions at a total concentration $\leq 25 \mu\text{g mL}^{-1}$ was transferred to a 50 mL separating funnel. The mixture was analyzed with AAS according to the described procedure for the extraction of tri-valent gold ions. Another aliquot portion (10 mL) was transferred and analyzed with AAS as described before for gold(I) determination. On the basis of these procedures, the amount of gold in the organic extract of the first aliquot (C_1) could be a measure of the gold(III) ions in the mixture, while the amount of gold in the organic extract of the second aliquot (C_2) is a measure of the sum of the mono- and tri-valent gold ions. Therefore, the difference ($C_2 - C_1$) is a measure of the gold(I) ions in the binary mixture.

2.4. Analytical applications

2.4.1. Analysis of gold(III) and total gold(I, III) in tap and wastewater samples

Tap and/or industrial wastewater samples (50 mL) of fertilizer industry were collected, filtered through a $0.45 \mu\text{m}$ membrane filter and the solutions pH were then adjusted to pH 6–7 with B–R buffer. To each of the sample solutions an accurate concentration of gold(I, III) species at a total concentration in the range $5.0\text{--}25.0 \mu\text{g Au mL}^{-1}$ and 2.0 mL of the reagent $\text{DPG}^+\cdot\text{Cl}^-$ ($8.0 \times 10^{-5} \text{ mol L}^{-1}$) were added. The solution mixtures were then transferred to 50 mL separating funnels. Analyze the mixtures according to the described procedure for gold(III). Another aliquot (50 mL) portions were taken exactly and analyzed as described for gold(I) species. On the basis of these procedures, the gold concentration determined by AAS in the first organic extract will be a measure of tri-valent gold ions in the mixture, while the amount of gold in the organic extract of the second aliquot is a measure of the sum of the gold(I) and (III) ions. Therefore, the difference between the two measure-

ments will be a measure of the mono-valent gold ions in the mixture.

2.4.2. Separation of gold(III) from silver(I) and base metal ions in tap water

An aliquot of tap water (10 mL) spiked with gold(III) ions in the concentration range $5.0\text{--}25.0 \mu\text{g mL}^{-1}$ Au was accurately transferred into a 50 mL separating funnel as described above. To the solution mixture, 2 mL containing silver(I) and/or base metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} or Zn^{2+}) at $10.0 \mu\text{g mL}^{-1}$ for each ion and few drops (0.2–0.3 mL) of KCl (1%, w/v) were added by the spiking method. The presence of KCl eliminates the possible interference of silver ions by forming AgCl precipitate. The solutions were then analyzed as described for gold(III) ions. The amount of gold(III) and base metal ions in the aqueous phase were determined with AAS from the standard curves of each ion at the optimum wavelength as described before.

3. Results and discussion

On mixing the reagent $\text{DPG}^+\cdot\text{Cl}^-$ with tetrachloro gold anion, AuCl_4^- in aqueous media and shaking with 4-methyl pentan-2-one, a yellow colored complex associate was developed in the organic phase. After equilibrium, the organic phase containing the complex ion associate of $\text{DPG}^+\cdot\text{Cl}^-$ and AuCl_4^- was separated out and its absorption electronic spectrum was then recorded. The spectrum showed one well-defined peak at 362 nm of the organic extracted while, the absorption spectrum of the reagent blank $\text{DPG}^+\cdot\text{Cl}^-$ against pure 4-methyl pentan-2-one showed no absorption peaks in the same wavelength range. On the absence of HAuCl_4 or $\text{DPG}^+\cdot\text{Cl}^-$ in the aqueous phase, no color or extraction of gold ions was detected in the organic layer as indicated from AAS measurement of gold ions in the organic or aqueous layer. Thus, each of $\text{DPG}^+\cdot\text{Cl}^-$ or AuCl_4^- separately did not extract in the organic phase. Therefore, in the subsequent work, the absorbance of the organic extract was measured at 362 nm against a reagent blank.

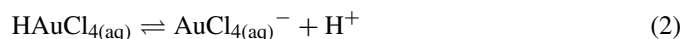
3.1. Investigation of the various experimental variables

Comparative tests of various organic solvents, e.g. *n*-hexane, dichloromethane, carbon tetrachloride, toluene, chloroform, diethyl ether, methyl ethyl ester, aromatic hydrocarbons and 4-methyl pentan-2-one with a wide range of functional group types was investigated for their ability to extract the produced complex associate. The data revealed that, the nature of the solvent contributes substantially to the maximum extraction of the produced complex ion associate of the $\text{DPG}^+\cdot\text{Cl}^-$ and AuCl_4^- ions. Good results were achieved with 4-methyl pentan-2-one and cyclohexanone and the absorbance of the organic phase followed the following order: 4-methyl pentan-2-one > cyclohexanone > ester > ether > dichloromethane > chloroform > toluene > carbon tetrachloride and *n*-hexane, respectively. The relatively high dielectric constant of these two solvents favors extensive ion-pairing formations [39]. Thus, the good extraction percentage (96–98%) with maximum apparent molar absorptivity, and solubility of the produced complex ion associate were

achieved. At room temperature, the extraction was complete in less than 2 min with better separation of phases in 4-methyl pentan-2-one. The reagent $\text{DPG}^+\cdot\text{Cl}^-$ in this solvent has no extraction and the colored complex ion associate was extracted quantitatively. The ion associate was found also stable for up to 2 h in this solvent. Thus, in the subsequent work, the solvent 4-methyl pentan-2-one was selected as a proper solvent. The amount of gold(III) extracted from the aqueous solution into the organic phase versus the amount of gold(III) in the aqueous phase at equilibrium varied linearly at low and moderate tri-valent gold(III) concentration ($\leq 10 \mu\text{g mL}^{-1}$) followed by a plateau at higher concentration. A solvent capacity of $5 \mu\text{g}$ gold(III) ions uptake per milliliter of organic solvent was obtained.

The optimum shaking time was ascertained by measuring the absorbance of the organic extract after 0.5–10 min shaking time. Rapid attainment of extraction equilibrium was achieved within 1.5–2 min. Thus, a 2 min shaking time was taken as the optimum time in the subsequent work to ensure complete extraction. The volume ratio of the aqueous phase ($5 \mu\text{g mL}^{-1}$ Au) to the organic phase ($V_{\text{(aq)}}^-/V_{\text{(org)}}^-$) was also examined for the extraction of gold ($5 \mu\text{g mL}^{-1}$ Au) species. For a single extraction, it was found that, quantitative extraction of gold was attainable up to 20-fold ($V_{\text{(aq)}}^-/V_{\text{(org)}}^- = 20:1$).

The effect of pH of the aqueous solution employing B–R buffer on the extraction of the developed colored complex ion associate was studied by measuring the absorbance of the organic extract at 362 nm against the reagent blank. Maximum absorbance of the produced ion associate was obtained at pH 5–9 (Fig. 2). In the aqueous solution of $\text{pH} \leq 5$, the ion pair $\text{DPG}^+\cdot\text{Cl}^-$ is less dissociated and gold(III) is most likely exists as chloroauric acid (HAuCl_4) species, which is less dissociated at lower pH as follows:



Thus, in acidic pH, the equilibrium (Eq. (2)) moves to the left and the quantity of AuCl_4^- ions available to form complex ion associate with $\text{DPG}^+\cdot\text{Cl}^-$ decreased. On the other hand, in aqueous solution of $\text{pH} \geq 9$, the absorbance of the organic extract also decreased. The formation of non-extractable com-

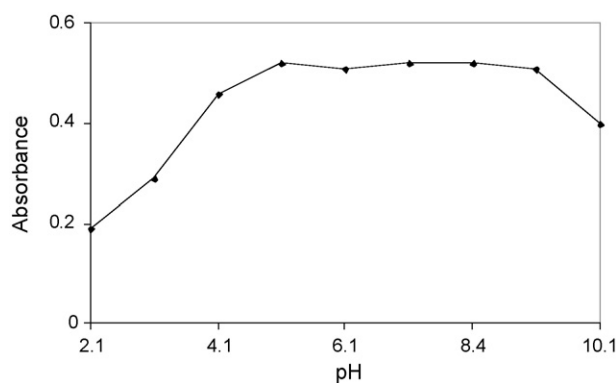
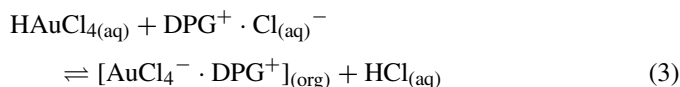


Fig. 2. Influence of pH on the uptake of the ion associate $[\text{DPG}^+\cdot\text{AuCl}_4^-]$ onto the solvent 4-methyl pentan-2-one (5 mL). Aqueous phase (20 mL) at pH 6–7, $\text{Au} = 2 \mu\text{g mL}^{-1}$ and 0.1 mL $\text{DPG}^+\cdot\text{Cl}^-$ (0.01%, w/v).

plex species of gold(III), e.g. hydroxo-species of gold(III) which minimizes the associate formation [40] may account for such trend. Thus, in the subsequent work the pH of the aqueous solution was adjusted at pH 6–7 and the overall reaction between $\text{DPG}^+\cdot\text{Cl}^-_{(\text{aq})}$ and $\text{HAuCl}_{4(\text{aq})}$ is most likely be proceeded as follows:



The influence of $\text{DPG}^+\cdot\text{Cl}^-$ concentration on the extraction of the formed ion associate at the optimum experimental conditions was studied. A 2 mL of $8.0 \times 10^{-5} \text{ mol L}^{-1}$ of $\text{DPG}^+\cdot\text{Cl}^-$ was found sufficient to extract quantitatively (96–98%) up to $10 \mu\text{g mL}^{-1}$ of gold(III) from the aqueous by double extraction ($2 \times 2.5 \text{ mL}$) of the organic solvent. The molar absorptivity of the produced ternary complex ion associate $\text{DPG}^+\cdot\text{AuCl}_4^-$ at 362 nm calculated from the absorbance measurement was found equal $2.19 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ in 4-methyl pentan-2-one. A large excess of the reagent slightly decreased the absorbance of the organic phase possibly owing to the increased acidity of the aqueous phase which minimizes the associate formation.

3.2. Effect of foreign ions

The selectivity of the developed method for the extraction of $5 \mu\text{g mL}^{-1}$ of tri-valent gold ions in the presence of a relatively high excess ($0.05\text{--}0.1 \text{ mg mL}^{-1}$) of some cations and anions was investigated. The tolerance limit was defined as the concentration of the foreign ion added causing a relative error within $\pm 2\%$ of the recovery of gold. It was found that, in the extraction of gold(III), the ions: Li^+ , Na^+ , K^+ , Ca^{2+} , NH_4^+ , Al^{3+} , Fe^{2+} , Ni^{2+} , Co^{2+} , Cu^{2+} and Zn^{2+} and the anions: Cl^- , Br^- , SO_4^{2-} , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$, PO_4^{3-} and $\text{S}_2\text{O}_8^{2-}$ do not interfere at 1:100 tolerable concentration of gold(III) to the diverse ions, respectively. Interference due to Fe^{3+} and VO_3^- and MnO_4^- (1:100, w/w) was eliminated by the addition of few drops of NaF (1%, w/v) and NaN_3 (0.1%, w/v) prior to the extraction, respectively. Interference of Ag^+ ions was removed by adding few drops of KCl (0.1%, w/v) to form AgCl precipitate. In the presence of some other ions, e.g. Pd^{2+} and Pt^{2+} even at low concentrations (1:10, v/v), positive interference was noticed. The ability of these ions to form extractable stable complex ion associates with the reagent $\text{DPG}^+\cdot\text{Cl}^-$ under the optimum experimental condition is most likely account for such behavior. These ratios do not induce limitations in the matrixes, e.g. salty effluents that could be analyzed by the developed extraction procedure.

3.3. Characterization of the gold(III) ion associates

The composition of the extracted species was determined at two different concentrations of the gold(III) ions and reagent by Job's method [41]. A plot of the absorbance of the organic extract at 362 nm versus the mole fraction of $\text{DPG}^+\cdot\text{Cl}^-$ revealed a graph that indicated the formation of an ion-association complex having gold(III) to a reagent molar

Table 1
Analytical results for the extraction of the binary mixture of mono- and tri-valent gold ions in aqueous media by the developed procedure

Gold species ($\mu\text{g mL}^{-1}$)		Recovery (%) ^a			
Gold(I) and (III) added		Average gold(I) and (III) found		Au ⁺	Au ³⁺
Au ⁺	Au ³⁺	Au ⁺	Au ³⁺		
5.0	10.0	4.9	10.3	98.0 \pm 2.7	103.0 \pm 2.7
10.0	15.0	9.7	15.2	97.0 \pm 2.2	101.3 \pm 2.3
15.0	10.0	14.8	10.2	98.7 \pm 2.1	102 \pm 1.6

^a Average recovery of five measurements \pm relative standard deviation.

ratio of 1:1. The organic extract was also evaporated under vacuum and analyzed for C, H, N and Au. The analytical data of the produced associate was found as follows: [AuOC₆H₉N₇Cl₅] required 12.62% C, 1.57% H, 17.24% N and 34.7% Au; Found 13.12% C, 1.76% H, 16.96% N and 35.23% Au. These data add further confirmation that, the extracted species are most likely represented as AuCl₄⁻·DPG⁺. The stability constant of the produced complex ion associate calculated from the Job's plot from the ratio of the true absorbance (*A*) to the extrapolated (*A*_{extp}) absorbance [41] was found equal to 2.46×10^3 .

A series of oxidizing agents such as H₂O₂, K₂S₂O₈ or bromine water has been tested for complete oxidation of mono-valence gold species to tri-valent gold species in aqueous media containing dilute acids (1 mol L⁻¹), e.g. CH₃COOH, HCl or H₂SO₄ or KCl (1 mol L⁻¹). Among these oxidizing agents, bromine water in HCl (1 mol L⁻¹) medium and boiling the aliquot aqueous solution of mono-valence gold species for 2 min was the most suitable oxidizing agent for gold(I) to gold(III) species. The oxidation performance of mono-valence gold to gold(III) species in the aqueous media followed the sequence:

bromine water > K₂S₂O₈ > H₂O₂

The variation of HCl concentration (0.1–2 mol L⁻¹) in the extraction media on the oxidation of gold(I) to gold(III) by bromine water and boiling was investigated following the same extraction procedure. The results revealed that optimum conditions for complete oxidation of gold(I) to gold(III) is to have an aqueous medium containing HCl (1 mol L⁻¹).

The extraction of gold(I) at concentration levels 1.0–15 $\mu\text{g mL}^{-1}$ after oxidation with Br₂ water in HCl (1 mol L⁻¹) and following the recommended extraction procedure for gold(III) was successfully achieved with a recovery percentage of $98 \pm 3.4\%$ ($n=5$). Thus, the analysis of the binary mixtures of gold(I) and (III) ions in the aqueous media by

the developed extraction procedure was attempted. The results are summarized in Table 1. Satisfactory recovery percentage of various gold(I) and gold(III) species was obtained.

3.4. Analytical applications

3.4.1. Chemical speciation and recovery of gold(I) and (III) from water samples

The validity of the developed extraction procedure was investigated by the determination of the mean percentage recoveries ($n=5$) of gold(III) in distilled water ((10 $\mu\text{g mL}^{-1}$ Au) using both the calibration graph and standard addition methods. The average percentage recoveries were found reproducible. The limits of detection (LOD) of gold(III) estimated using the equation: $\text{LOD} = 3S_{y/x}/b$ [42]; where $S_{y/x}$ is the standard deviation of *y*-residuals and *b* is the slope of the calibration plot was found equal 6.1×10^{-7} . The value of the lower limit of quantification (LOQ) calculated using the equation: $\text{LOQ} = 10S_{y/x}/b$ [42], was found equal 9.2×10^{-7} mol L⁻¹. This level of precision is suitable for the routine analysis of the gold(III) in water.

The application of the developed extraction procedure for the chemical speciation and recovery of traces of gold(I) and (III) at a total concentration $\leq 25.0 \mu\text{g mL}^{-1}$ in tap water was investigated as described in Section 2. A recovery percentage of 97 ± 2.9 was achieved with good reproducibility. Thus, attempts were also applied for the analysis of gold(I, III) in wastewater samples of fertilizer industry following the described experimental procedure. The data are summarized in Table 2. The accuracy of the developed procedure was evaluated by the recovery studies of the gold added. Also, on plotting the amount of gold added versus the amount recovered a regression line with a slope of 0.998 and a correlation coefficient of 0.999 was achieved. The slightly higher values of recoveries in the wastewater may be due the presence of other impurities in the wastewater (Table 2). The *F*-test at 95% confidence levels did not exceed the tabulated (the-

Table 2
Analytical results of the chemical speciation and recovery of mono- and tri-valent gold ions in wastewater samples by the proposed extraction procedure

Gold species ($\mu\text{g mL}^{-1}$)		Recovery (%) ^a			
Gold(I) and (III) added		Average gold(I) and (III) found		Au ⁺	Au ³⁺
Au ⁺	Au ³⁺	Au ⁺	Au ³⁺		
5.0	10.0	4.8	10.4	96.0 \pm 2.4	104.0 \pm 2.9
10.0	15.0	9.7	15.2	97.0 \pm 2.8	101.3 \pm 2.1
15.0	15.0	14.8	14.8	98.7 \pm 3.1	98.7 \pm 1.9

^a Average of five measurements \pm relative standard deviation.

Table 3

Analytical results of the recovery of Au^{3+ss} (5–15 µg mL⁻¹) from Ag⁺ and other metal ions, e.g. Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ or Zn²⁺ at 10.0 µg mL⁻¹ interfering in tap water samples by the proposed procedure

Gold(III) added (µg mL ⁻¹)	Gold(III) found (µg mL ⁻¹)	Recovery (%) ^a
5.0	5.15	103 ± 2.1
10.0	10.35	103.5 ± 1.9
15.0	14.8	98.7 ± 2.1

^a Average of three measurements ± relative standard deviation.

oretical) ones and revealed no significant differences between the averages and the variances of the developed procedure and the reported method [30].

3.4.2. Separation of gold(I) and (III) from silver(I) and other base metal ions

The developed extraction procedure was also applied successfully for the separation of gold(III) ions in the concentration range 5–15.0 µg mL⁻¹ Au from silver(I) and base metal (Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ and Zn²⁺) ions at 10.0 µg mL⁻¹ level in tap water samples. The results are summarized in Table 3. More or less complete recovery of gold ions was achieved with good precision (R.S.D. ≤ 2.1%). In terms of *F* (0.075) and Student's *t* tests (1.91), no significant differences in the accuracy and precision [42] between the proposed and the published method [31] were observed.

4. Conclusion

The method provides an excellent alternative approach for the analytical determination of gold because of its low cost, repeatability and sufficient precision. The reaction of the reagent DPG⁺·Cl⁻ with the anion AuCl₄⁻ is rapid, simple, does not involve any stringent conditions and no standing time is needed. The produced ternary complex ion associate DPG⁺·AuCl₄⁻ is stable before determining the ions. Thus, the developed extraction procedures was also applied for the extraction and subsequent AAS determination of inorganic gold(I) and/or (III) ions in fresh and industrial wastewater samples after oxidation of the former ion to gold(III) with bromine water. The procedures have the advantage of virtual freedom from most interfering ions and can serve as a low cost procedure for the separation of gold from silver and base metal ions. However, work is continuing for the recovery of gold species from different matrixes and application of on line procedures for the chemical speciation of inorganic and organic bound gold species in reference and real samples.

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