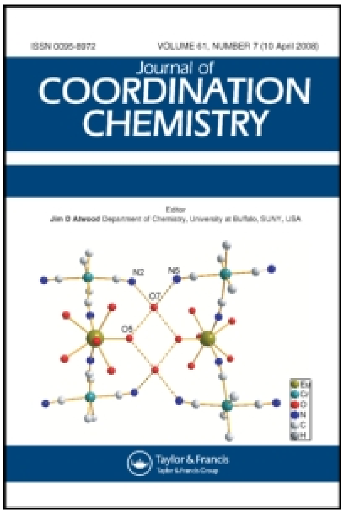

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Selective extraction and determination of Au(III) by first-derivative spectrophotometry

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Selective extraction and determination of Au(III) by first-derivative spectrophotometry

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The selective extraction of Au(III) in the presence of Zn(II) by salting-out of 2-propanol was investigated. The salting-out effect increased partitioning between water and 2-propanol in the presence of sodium chloride in aqueous–organic mixtures. This is observed through the distribution coefficient, which increases with salt addition. First-derivative spectrophotometry, which eliminates interference from overlapping spectral bands, was used for the determination of trace Au(III) in the presence of Zn(II). Absorption spectra were recorded and the first-derivative spectra were obtained using $\Delta\lambda = 10\,\text{nm}$. The calibration graph was linear for 0.857–5.142 $\mu\text{g mL}^{-1}$ and the detection limit was 0.038–8 $\mu\text{g mL}^{-1}$. The proposed method has been successfully applied to the determination of trace Au(III) in synthetic mixtures and Algerian low gold ore solutions. The results agree with those obtained by atomic absorption spectroscopy and the recoveries were >98%. The relative standard deviations were in all instances less than 3%.

Keywords: Solvent extraction; Salting-out; Au(III); Zn(II); First-derivative spectrophotometry

1. Introduction

Over the past three decades, theory and application of metal extraction have greatly advanced with selective separation of valuable metals, an area of considerable interest [1–6]. The literature survey reveals several selective extractants that have been used to remove metal ions from different media [7–10]. The solvent extraction of gold is mainly performed using cyanide leaching. However, research efforts have been directed toward the use of noncyanide processes for recovery of gold due to the increasing concern regarding the hazardous character of cyanide [11–19]. Commercial extractants containing phosphine oxides [20, 21], amines [22], thiophosphinic acids [23], and calixarene derivatives [24] were investigated with respect to Au(III). Spectrophotometric determination of gold in water and ore with 2-carboxyl-1-naphthalthiorhodanine was studied by Chen *et al.* [25]. Three derivatives of dibutylphosphonic acid, α,α'-*bis*(dibutylphosphonatol)-l,3-xylene and *bis*(dibutylphosphonato)alkanes, commonly known as the tetrabutyl 1,3-xylylenediphosphonate (TBmXDP) and tetrabutyl alkylenediphosphonates (TBADP), respectively, were synthesized by Chowdhury and

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Kamata [26] for use in solvent extraction of precious metals, especially Au(III) extraction from hydrochloric acid medium. Dodecyl-thiourea (DTH), which has been used as extractant for Au(III) in the presence of Cu(II) and Fe(III), was investigated by Zuo and Muhammed [27]. The Au(III)–DTH extraction data were explained by the formation of $AuCl_3 \cdot (DTH)_3$. Akita *et al.* [28] have applied the cloud-point extraction technique to recovery of gold from an aqua regia leaching solution of a printed substrate, and an overall process, including stripping and reduction steps, was proposed. Some of these extractants are expensive and have disadvantages, such as low extraction power from strongly acidic solutions, difficult back extraction and loss of reagent, low selectivity, slight solubility in water, or degradation during use. Conventional solvent extraction has involved the use of solvents, such as chloroform and benzene.

Phase separation occurs from mixed water and water-miscible organic solvents upon the addition of electrolytes to the mixed solvents. The salting-out is due to decreased solubility of organic solvents in water in the presence of electrolytes [29]. The salting-out effect on liquid–liquid equilibria has been the topic of investigation in separation processes [30–32].

First-derivative spectroscopy using zero-crossing has been applied successfully for simultaneous determination of metal ions in their binary mixture [33–39]. Toral and Richter [40] developed a spectrophotometric method for the determination of copper and iron in mixtures. This method is based on the recovery of the analytes, by liquid–liquid extraction, integrated reaction with 5-phenyl-3-(4-phenyl-2-pyridinyl)-1,2,4-triazine (PPT) and perchlorate in dichloroethane and on the subsequent direct derivative spectrophotometric measurement using the zero-crossing approach for the determination of both analytes. Simultaneous determination of Pd(II) and Ru(III) using second-order derivative spectrophotometry was studied by Praveen Kumar *et al.* [41]. Pd(II) and Ru(III) present in the mixture were simultaneously determined without solving the simultaneous equations by measuring the second derivative amplitudes at 445 and 385 nm, respectively. The proposed method was successfully applied for the determination of palladium in hydrogenation catalysts and ruthenium in water samples. Fourth-order derivative spectrophotometric procedure was also developed by Jyothi *et al.* [42] for the determination of traces of cobalt based on liquid–liquid extraction of ternary ion – association complex – cobalt, 1,10-phenanthroline, rose bengal into chloroform. The developed procedure allows determination of cobalt as low as 6 ppb in high purity rare earth oxides and salts.

In this study, batch salting-out experiments were performed with the objective to know more about the limits and possibilities on selective extraction of gold in the presence of zinc into 2-propanol by the salting-out method using sodium chloride to cause phase separation. First-derivative spectrophotometric method for the determination of Au(III) in the presence of Zn(II) is described.

2. Experimental

2.1. *Reagents*

The concentration of hydrochloric acid was always maintained at $0.1\,mol\,L^{-1}$ and the concentration range of NaCl was $0.5–4.0\,mol\,L^{-1}$ under the salting-out conditions.

The initial concentration of metal ions was varied from 0.857 to 5.999 μg mL^{-1} for Au(III) and from 0.272 to 4.88 μg mL^{-1} for Zn(II). Aqueous solutions of metal ions were prepared by dilution of the standard metal chloride solutions ($AuCl_3$ and $ZnCl_2$) in 0.1 mol L^{-1} HCl. A 10^{-2} mol L^{-1} of dithizone (DTZ) was prepared from the pure product (Labosi) by dissolving an appropriate weight in 50 mL of propanol. A 10^{-3} mol L^{-1} of cetylpyridinium chloride (CPC) aqueous solution was prepared from the pure product (Labosi) by dissolving an appropriate weight in 25 mL of distilled water. A buffer of pH 4 was prepared using sodium acetate and acetic acid at appropriate concentrations. All commercial reagents used were of analytical grade and distilled water was used for the preparation of mother solutions. The 2-propanol (99.97%, Labosi) was used without purification. NaCl (Labosi) was dried in an electric oven at 300°C for 2 h.

2.2. *Experimental procedure*

Solvent extraction experiments were carried out in a volume-calibrated graduated tube immersed in a thermostated water bath (±0.1°C) using equal volumes (5 mL) of the organic and the aqueous phases containing 0.1 mol L^{-1} hydrochloric acid in the presence of different concentrations of sodium chloride and 2-propanol. The extraction equilibrium was reached after 30 min under continuous magnetic stirring. After separation of the two phases, the concentration of the metal remaining in the aqueous phase was measured. Metal contents before and after extraction were analyzed by means of atomic absorption spectroscopy (AAS; Shimadzu AA 6500). In most cases, the precision of AAS measurements indicated errors smaller than 1%. The results found are the mean of five separate measurements. Equilibrium pH values were measured with a combination glass electrode (Schott N42) after extraction and phase separation.

The distribution coefficient and (%E) were calculated according to equations (1) and (2):

$$D = \frac{[M]_{\text{org}}}{[M]_{\text{aq}}}, \tag{1}$$

where $[M]_{\text{aq}}$ and $[M]_{\text{org}}$ represent the total concentrations of the metal ion that has equilibrated in the organic and aqueous phases, respectively, and $[M]_{\text{in}}$ is the initial concentration before extraction. The percentage of metal extraction was calculated using equation (2).

$$\%E = \frac{[M]_{\text{in}} - [M]_{\text{aq}}}{[M]_{\text{aq}}} \,.\, 100\% \tag{2}$$

A Shimadzu UV-2101PC double beam UV-Vis spectrophotometer with a fixed slit width of 0.5 nm and its recorder were used. Derivative spectra were recorded with a slit width $\Delta\lambda = 10$ nm calculated by the method of Savittzky and Golay [43]. The determination of Au(III) as Au(III)–DTZ–CPC in the presence of Zn(II) complexes using first-derivative spectrophotometry (FDS) was investigated. A 5 mL buffer solution, a 3 mL of DTZ, and an appropriate volume of Au(III) or Zn(II) were added to a 10-mL volumetric flask and made up to the mark with redistilled water. The first-order derivatives of these spectra were recorded over the 400–800 nm wavelength

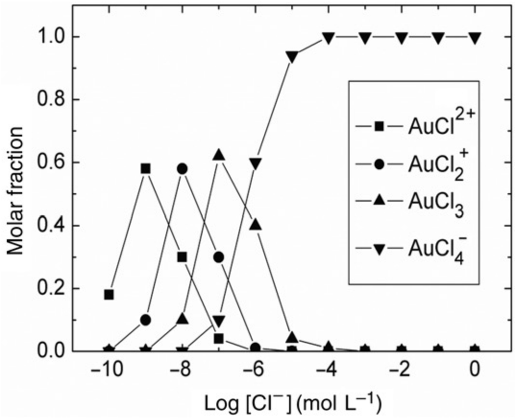

Figure 1. Effect of chloride concentration on the formation of chemical species of Au(III) in aqueous solutions.

range, and the amplitudes were measured at 445 and 438 nm for Au(III) and Zn(II), respectively.

3. Results and discussion

3.1. *Effect of chloride concentration on the formation of chemical species of Au(III) in aqueous solution*

The formation of Au(III) chloro complexes in various chloride concentrations is shown in figure 1. The effect of sodium chloride concentrations in aqueous solution was examined.

The addition of NaCl leads to the formation of chloro complexes, phase separation between water and 2-propanol, and provides counter ions to the extracted ionic species. NaCl makes the 2-propanol phase highly polar compared to pure 2-propanol [29]. At high chloride concentration, greater than 3.0 mol L^{-1}, Au(III) under these experimental conditions exists predominantly as $[AuCl_4]^-$ and can be extracted quantitatively into organic phase. $[AuCl_4]^-$ is tetrahedral and the coordination sites of Au(III) are fully occupied by chloride, so that water does not bind to $[AuCl_4]^-$. Hence, the extractability of Au(III) is very high at 4.0 mol L^{-1}.

3.2. *Effect of chloride concentration on percentage extraction of Au(III) and Zn(II)*

Figure 2 shows the effect of NaCl concentrations on the percentage extraction of gold and zinc. Extraction of gold as $[AuCl_4]^-$ increases with increasing concentration of NaCl in the organic phase. Selective extraction of gold over zinc is obtained at 4 mol L^{-1} NaCl. In that case, $[AuCl_4]^-$ ions were transferred into organic phase by

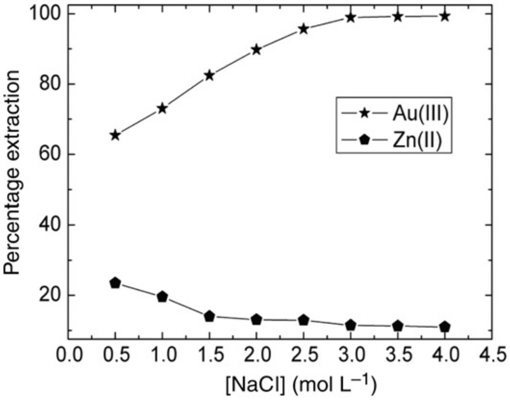

Figure 2. Effect of chloride concentration on percentage extraction of Au(III) and Zn(II).

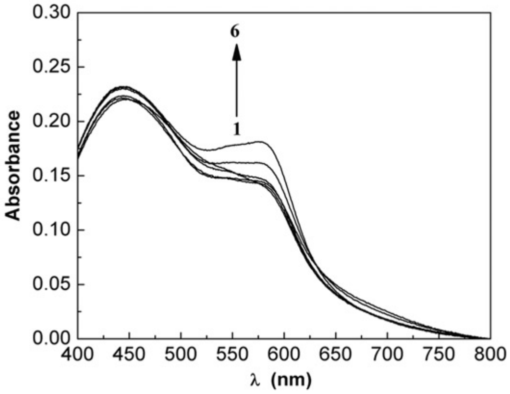

Figure 3. Zero-order spectra of Au(III)–DTZ–CPC and increasing concentrations of Zn(II). [Au(III)] = 10^{-4} mol L^{-1}, [DTZ] = 4×10^{-4} mol L^{-1}, [CPC] = 10^{-4} mol L^{-1}, [Zn(II)] = (1) 0.272, (2) 0.545, (3) 1.090, (4) 1.635, (5) 2.180, and (6) 2.725 μg mL^{-1}; pH = 4.

formation of ion-pair complexes with Na(I). The possible mechanism of extraction of Au(III) in the mixture of 2-propanol and water is given by equation (3):

$$\mathrm{Au}^{3+}_{\mathrm{aq}} + 4\mathrm{Cl}^- + \mathrm{Na}^+ \rightarrow \left[\mathrm{AuCl}_4^- \cdot \mathrm{Na}^+\right]_{\mathrm{org}}. \qquad (3)$$

3.3. *Zero-crossing first-derivative spectrophotometric determination of Au(III) in the presence of Zn(II)*

To determine concentrations in aqueous phase, a simple, rapid, and sensitive spectrophotometric method for the determination of trace amounts of Au(III) in the presence of Zn(II) based on first-derivative spectroscopy using zero-crossing was investigated. Figures 3 and 4 show the zero-order spectra of mixtures of Au(III)–DTZ–CPC and Zn(II)–DTZ–CPC in the wavelength range 400–800 nm.

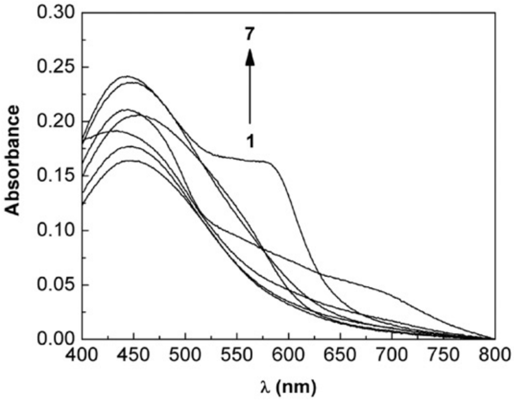

Figure 4. Zero-order spectra of Zn(II)–DTZ–CPC and increasing concentrations of Au(III). $[\mathrm{Zn(II)}] = 10^{-4}\,\mathrm{mol\,L^{-1}}$, $[\mathrm{DTZ}] = 4\times10^{-4}\,\mathrm{mol\,L^{-1}}$, $[\mathrm{CPC}] = 10^{-4}\,\mathrm{mol\,L^{-1}}$, [Au(III)] = (1) 0.857, (2) 1.714, (3) 2.571, (4) 3.428, (5) 4.285, (6) 5.142, and (7) $5.99\,\mu\mathrm{g\,mL^{-1}}$; pH = 4.

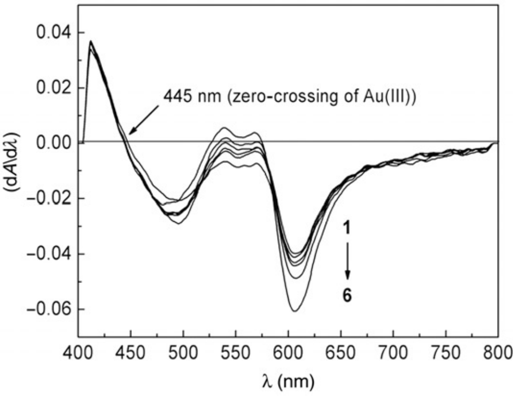

Figure 5. First-derivative spectra of Zn(II)–DTZ–CPC and increasing concentrations of Au(III). $[\mathrm{Zn(II)}] = 10^{-4}\,\mathrm{mol\,L^{-1}}$, $[\mathrm{DTZ}] = 4\times10^{-4}\,\mathrm{mol\,L^{-1}}$, $[\mathrm{CPC}] = 10^{-4}\,\mathrm{mol\,L^{-1}}$, [Au(III)] = (1) 0.857, (2) 1.714, (3) 2.571, (4) 3.428, (5) 5.142, and (6) $5.999\,\mu\mathrm{g\,L^{-1}}$; pH = 4.

The amplitudes were measured at 445 and 438 nm for Au(III) and Zn(II), respectively. There is clear overlapping of the spectra, in that case, a simultaneous determination of Au(III) and Zn(II) by direct UV-Vis absorbance measurements is difficult. The application of derivatization enables separation of hidden signals and uses them for quantitative purposes. Figure 5 shows the first-derivative spectra of Zn(II)–DTZ–CPC with increasing concentrations of Au(III). The zero-crossing of Au(III) was obtained when $\mathrm{d}A/\mathrm{d}\lambda = 0$. So, the concentration of Au(III) was determined by measuring the amplitudes at 606.01 nm when the first-derivative mode was applied.

The calibration graph, figure 6, was constructed between 0.857 and $5.142\,\mu\mathrm{g\,mL^{-1}}$ under the optimal conditions using the value of derivative amplitude versus concentration of Au(III). The concentrations of Au(III) can be estimated from the linear calibration curve of first-derivative absorbance values ($\mathrm{d}A/\mathrm{d}\lambda$) *versus*

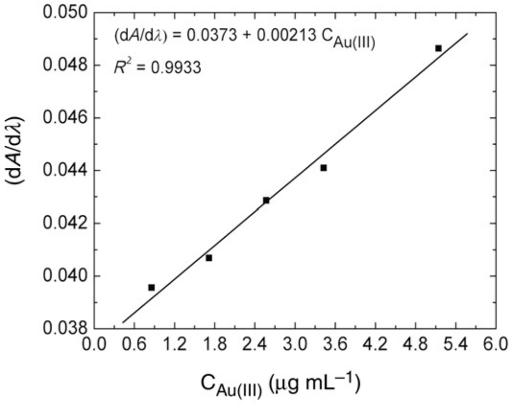

Figure 6. Calibration graph for Au(III) determination by first-order derivative spectrophotometry in the presence of Zn(II). Concentrations of Au(III) varied between 0.857 and 5.142 μg mL^{-1}, and the amplitudes were measured at 606.01 nm.

Table 1. The results of analyses of Au(III) in synthetic mixture low gold ore solution by a different analyst.[a]

	Proposed method (FDS)	AAS
Sample	Au(III) (μg mL^{-1})	Au(III) (μg mL^{-1})
Synthetic mixture	2.67 ± 0.35	2.61 ± 0.29
Low gold ore solution	5.36 ± 0.37	5.29 ± 0.31

FDS, first-derivative spectrophotometry and AAS, atomic absorption spectrometry.

[a] The results found are mean five separate measurements.

concentration ($C_{Au(III)}$). The calibration curve for Au(III) using the first-derivative values has the following equation:

$$(dA/d\lambda) = 0.03732 + 0.00213\ C_{Au(III)}. \quad (4)$$

From the obtained equation, the limit of detection was 0.038 μg mL^{-1} and the correlation coefficient was $R^2 = 0.9933$. To estimate the precision (relative standard deviation (RSD)) of the method, replicate samples ($n = 5$) were measured individually. The proposed method has been successfully applied for the determination of trace of Au(III) in synthetic mixtures and Algerian low gold ore solutions. The results are given in table 1. Good agreement was achieved between the results obtained by our comparative methods.

4. Conclusion

The extraction of Au(III) by 2-propanol over Zn(II) was investigated. The results obtained from the experiments showed that the concentration of electrolyte significantly affects the percentage extraction. At high chloride concentration (greater than $3\,\mathrm{mol\,L^{-1}}$) Au(III) under these experimental conditions exists predominantly as $[\mathrm{AuCl_4}]^-$, coordination sites of Au(III) are fully occupied by chloride, so water does not bind to $[\mathrm{AuCl_4}]^-$. Hence, the selective extractability of Au(III) over Zn(II) is high at $4\,\mathrm{mol\,L^{-1}}$ NaCl with RSDs lower than 3%. Using salting-out approach in sample pretreatment may provide a new alternative for a laboratory experiencing difficulties in establishing an analysis method. First-derivative spectrophotometric method for the determination of Au(III) in the presence of Zn(II) is described. This method is based on the colored complex formed by Au(III) and DTZ in the presence of CPC as a surfactant. The zero-crossing method has been utilized to measure the first-derivative value of the derivative spectra. The calibration graph was linear for 0.857–$5.142\,\mu\mathrm{g\,mL^{-1}}$ and the detection limit was 0.038–$8\,\mu\mathrm{g\,mL^{-1}}$. The proposed method has been successfully applied for the determination of trace Au(III) in synthetic mixtures and Algerian low gold ore solutions. The proposed method is suitable for routine analysis. The procedure is simple, rapid, and reliable.

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