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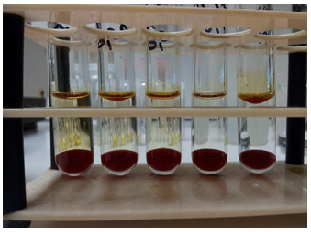
$$AuX_4^-{}_{(w)} + C^+A^-{}_{(IL)} \rightleftharpoons C^+AuX_4^-{}_{(IL)} + A^-{}_{(w)}$$



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Efficient extraction of gold from water by liquid-liquid extraction or precipitation using hydrophobic ionic liquids.

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Extraction of tetrachloroaurate or tetrabromoaurate anions has been carried out with several ionic liquids bearing trialkyl(2-ethoxy-2-oxoethyl)ammonium (with alky group = C_2H_5 [$EtGBOEt^+$], n-C_3H_7 [$PrGBOEt^+$] or n-C_4H_9 [$BuGBOEt^+$]) cations and halide (Cl^- or Br^-), bis(trifluoromethanesulfonyl)imide (Tf_2N^-) and dicyanamide (Dca^-) anions. The removal of gold anionic moieties from water was first studied by mixing aqueous solutions containing gold complexes and water soluble bromide ionic liquids. This led to the formation of a solid precipitate corresponding to hydrophobic ionic liquid based on a tetrahalogenoaurate anion. Liquid–liquid extraction of anionic gold complexes with hydrophobic ionic liquids was also investigated.

Introduction

Ionic liquids (ILs) are solvents constituted by ion pairs. These organic salts, with a low melting point, are considered as green solvents because of their specific physicochemical properties (non-flammability, low vapour pressure).[1-3] The replacement of conventional solvents by ionic liquids offers clear advantages, therefore, the scope of ionic liquids gradually has grown up over the last twenty years particularly in the field of electrochemistry and catalysis.[4] In the last decade, significant works have highlighted the potential of hydrophobic room temperature ionic liquids (RTILs) as substitute to traditional solvents, used in liquid-liquid extraction processes, for the separation of metal ions.[5-7]. The liquid-liquid extraction is one of the efficient techniques to separate and concentrate metal ions from industrial wastewater. The major drawback of this technique is the loss of organic diluent *via* volatilisation, which has a detrimental impact on the environment and human health. Consequently, "greener" extraction methods are required and the use of ILs as alternatives to traditional organic solvents could overcome this disadvantage[8]. Since ionic liquids are more expensive than traditional solvents, their use in commercial processes is rather limited particularly in processes where large quantities of solvent are required. However the development of cost-effective ILs should render their use appropriate for industrial applications, in particular for the recovery of high-value metals from ore leaching. Recently, several studies have evidenced the potential of ILs for the treatment of ore leaching and the recovery of precious metal such as Pt(II), Pd(II) and Au(III).[9-16] Among these metals, gold is an important high value metal. Recently, the application of 1-butyl-3-methyl-imidazolium hydrogen sulphate or analogue ILs as solvent media to leach of gold-bearing ores have been attempted and some advantages of this methodology, such as the recyclability of ionic liquids have been demonstrated .[9,10] Other ILs based on some organic cations (pyridinium, pyrrolidinium, and methylimidazolium) have been also developed as carriers for extraction of noble metal ions from aqueous solution, including Au(III) with a good efficiency. These studies open the door to the development of greener methodologies which will in the long term, allow the substitution of the organic solvents and cyanide salts used for the recovery of precious metals.

In this objective, we report the ability of task-specific ionic liquids to extract tetrahalogenoaurate ions ($AuCl_4^-$ or $AuBr_4^-$) from aqueous effluents. The studied ILs were generated by association between a cationic ester derivative of betaine tri(n-alkyl)[2-ethoxy-2-oxoethyl)ammonium ($RGBOEt^+$ with R = C_2H_5, n-C_3H_7 or n-C_4H_9) and anions commonly used to generate ionic liquids such as bis(trifluoromethylsulfonyl)imide (Tf_2N^-) and dicyanamide ($(NC)_2N^-$ = Dca^-). In a previous study, we showed the ability of such ionic liquids to extract metal ions[17,18]. In this work, we completed our investigations by evaluating the potential of these ILs as extracting agents for the high value metals such as Au. The choice of the betaine derivative is justified by its accessibility *via* simple synthetic route, by its availability, the cost of starting materials, and its structural modularity, which allows the control of the cation hydrophobicity by varying the alkyl chain length bound to ammonium group. Two different methods are investigated to remove AuX_4^- from water. Firstly, the precipitation of AuX_4^-, from an aqueous phase, with an organic cation from water soluble ILs [$EtGBOEt^+$][Br^-], [$PrGBOEt^+$][Br^-] and [$BuGBOEt^+$][Br^-] is reported. Secondly, the liquid-liquid extraction of AuX_4^- from an aqueous solution using hydrophobic ILs [$BuGBOEt^+$][Tf_2N^-], [$EtGBOEt^+$][Tf_2N^-] or [$BuGBOEt^+$][Dca^-] was investigated. In order to develop and better understand the extraction process, we have studied the fundamental aspect of the metal transfer from the aqueous phase to the IL phase taking into account the hydrophobicity of the organic cation and the nature of the IL anions.

The coordination of Au(III) in the IL phase was also investigated by UV-vis spectroscopy.

Results and discussion

Synthesis

The ILs were synthesized by a two-step procedure described previously.[17] All syntheses were done with the same experimental conditions. The cationic esters derivatives of betaine triethyl[(2-ethoxy-2-oxoethyl]ammonium bromide ([EtGBOEt$^+$][Br$^-$]), tri(*n*-propyl)[(2-ethoxy-2-oxoethyl]ammonium bromide ([PrGBOEt$^+$][Br$^-$]) and tri(*n*-butyl)[(2-ethoxy-2-oxoethyl]ammonium bromide ([BuGBOEt$^+$][Br$^-$]**)** were successfully synthesized by the reaction of ethyl 2-bromoacetate and triethylamine, tri(*n*-propyl)amine or tri(*n*-butyl)amine, respectively.[17] The association of [BuGBOEt$^+$][Br$^-$] and [EtGBOEt$^+$][Br$^-$] with NaDca or LiTf$_2$N generates hydrophobic ILs by anionic metathesis, ([EtGBOEt$^+$][Tf$_2$N$^-$], [BuGBOEt$^+$][Tf$_2$N$^-$] or [BuGBOEt$^+$][Dca$^-$]) in quantitative yield (figure 1).
The association of [PrGBOEt$^+$][Br$^-$] with LiTf$_2$N generates a solid IL which was used only for precipitation experiments. The associations between [EtGBOEt$^+$][Br$^-$] and [PrGBOEt$^+$][Br$^-$] with NaDca generate hydrophilic ILs which were not considered in this study. The various ILs obtained were solubilized in ethyl-acetate and recovered by evaporation under vacuum. The resulting oils were washed with distilled water until no bromide impurities are detected in aqueous phase, with an AgNO$_3$ test, and then freeze-dried. Their purity was checked by nuclear magnetic resonance spectroscopy and C, H, N elemental analysis.[17]

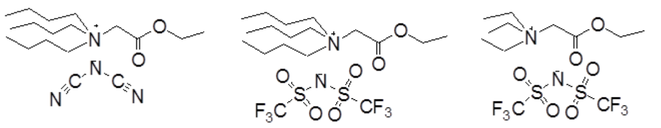

Figure 1 : structure of trialkyl(2-ethoxy-2-oxoethyl)ammonium based ionic liquids

Precipitation of tetrahalogenate-based ionic liquids

Precipitation experiments are similar to a metathesis reaction leading to the formation of an hydrophobic ionic liquid phase or a precipitate constituted by ion-pair [AlkylGBOEt$^+$][AuX$_4^-$]
The reaction can be written as follows:

$$\text{AlkylGBOEt}^+_{w} + \text{AuX}_4{}^-_{w} \rightleftharpoons [\text{AlkylGBOEt}^+]_{IL}[\text{AuX}_4^-]_{IL} \qquad (1)$$

The compound [AlkylGBOEt$^+$]$_{IL}$[AuX$_4^-$]$_{IL}$ corresponds to the precipitate formed or the liquid phase at the bottom of the tube. The solubility products of [AlkylGBOEt$^+$]$_{Il}$[AuCl$_4^-$]$_{Il}$ ionic liquids are written as follows :

$$K_{Au} = [\text{AlkylGBOEt}^+]_w[\text{AuX}_4^-]_w \qquad (2)$$

where [AlkylGBOEt$^+$]$_w$ and [AuX$_4^-$]$_w$ are the concentrations of organic cation and tetrahalogenoaurate anion in aqueous solution after precipitation. The concentration of organic cation ([AlkylGBOEt$^+$]) was deduced from its initial concentration before precipitation ([AlkylGBOEt$^+$]$_{initial}$), determined from sulphur analysis by ICP-OES, and the amount of AuCl$_4^-$ consumed by the precipitation.

$$[AlkylGBOEt^+]_w = [AlkylGBOEt^+]_{initial} - ([AuX_4^-]_{initial} - [AuX_4^-]_w) \quad (3)$$

The concentrations of AuCl$_4^-$ and AuBr$_4^-$ were determined by UV-vis spectroscopy.

The average values for pK$_{Au}$ for [EtGBOEt$^+$][AuX$_4^-$], [PrGBOEt$^+$][AuX$_4^-$], [BuGBOEt$^+$][AuX$_4^-$], (X = Cl$^-$ or Br$^-$) are reported in Table 1. In order to allow the interpretation of the obtained results, the values of solubility product of IL with Tf$_2$N$^-$ and Dca$^-$ anions (see below) were also reported. These results reveal that the ILs containing AuX$_4^-$ are practically immiscible in water (solubility ranging from 5×10^{-6} to 5×10^{-3} mol L^{-1}). For the same anion, the solubility of [AlkylGBOEt$^+$][AuX$_4^-$] ionic liquid decreases as the length of alkyl chain of the cation (hydrophobicity) increases. With the same cation, the AuBr$_4^-$ ILs are less soluble than those containing AuCl$_4^-$. The ionic crystallographic radius of bromide and chloride are 3.92 Å and 3.62 Å, respectively[19]. So, AuBr$_4^-$ is expected to be larger and softer than AuCl$_4^-$; the larger the ion, the lower the charge density and the solvation energy (weaker ion-solvent) interaction[20]. This explains the lower solubility of the AuBr$_4^-$ ILs compared to the AuCl$_4^-$ ILs.

Table 1 : Solubility products (pK$_{Au}$) of [AlkylGBOEt$^+$][AuX$_4^-$] and (pK$_{IL}$) of [AlkylGBOEt$^+$][Tf$_2$N$^-$] and [AlkylGBOEt$^+$][Dca$^-$]compounds (Alkyl = ethyl or *n*-butyl)

	AuCl$_4^-$	AuBr$_4^-$	Tf$_2$N$^-$	Dca$^-$
[EtGBOEt$^+$]	4.6 (0.1)	6.6(0.1)	3.4 (0.1)	-
[BuGBOEt$^+$]	5.2 (0.1)	10.3 (0.1)	5.7 (0.1)	3.5 (0.1)

Values in parentheses refer to estimated uncertainty

These results show that the direct use of [AlkylGBOEt$^+$][Br$^-$] hydrophilic IL can be a good alternative for removing gold from water by the formation of [AlkylGBOEt$^+$][AuX$_4^-$] giving an immiscible phase. The results for precipitation experiments using bromide salt of [AlkylGBOEt$^+$] cations are given in Table 2 and pictures of an intense yellow or orange precipitate obtained are depicted in figure 2. The precipitates, isolated for a ratio ([AlkylGBOEt$^+$][Br$^-$])/Au) = 10, have been analysed. For the three studied systems, elemental analysis (ESI) reveals a partial or total substitution of chloride anions by bromide anions. Indeed, the stoechiometries of precipitates correspond to [PrGBOEt$^+$][AuClBr$_3^-$], [BuGBOEt$^+$][AuClBr$_3^-$] and [EtGBOEt$^+$][AuBr$_4^-$]. In aqueous solution AuCl$_4^-$ anion exhibits a square planar geometry and its UV-vis spectra show a specific absorption with a maxima at 313 nm due to a ligand (π)-metal (σ*) charge transfer (LMCT) transitions[21]. The spectrum of AuBr$_4^-$ shows two transitions with maxima at 380 nm and 254 nm. The band at 380 nm has a shoulder at 450 nm. The substitution reaction of chloride by bromide ion is justified by the softer character of the latter, leading to the formation of Au^{III}-Br bonds with higher stability.

Figure 2 : Snapshots of precipitate taken after mixing [AlkylGBOEt$^+$][Br$^-$] with HAuCl$_4$..

This substitution reaction was studied by Usher *et al.*[21] in aqueous solution. According to their study, the progressive substitution of chloride ions by bromide one induces a gradual shift of the LMCT transition from 313 nm ($AuCl_4^-$) to 380nm ($AuBr_4^-$). The molar absorbance of all the intermediate $AuCl_xBr_{(4-x)}^-$ (x = integer and 1 ≤ x ≤ 4) complexes have been resolved. In our case, the UV-Vis spectra of the precipitates $[BuGBOEt^+][AuClBr_3^-]$, $[PrGBOEt^+][AuClBr_3^-]$ and $[EtGBOEt^+][AuBr_4^-]$, dissolved in ethyl acetate, show only one transition in the region 300-500 nm, with a maxima at 355, 363 and 378 nm, respectively (figure 3). This means that these precipitates correspond more likely to complexes of $AuCl_xBr_{(4-x)}^-$ stoechiometry rather than a mixture between $[AlkylGBOEt^+][AuCl_4^-]$ and $[AlkylGBOEt^+][AuBr_4^-]$ in variable proportion. For all $[AlkylGBOEt^+][AuX_4^-]$ precipitates, the location of the maximum of the absorbance corroborates the stoechiometry of the complexes deduced from elemental analysis.

Table 2 : Extraction efficiency of gold complexes (%E) in water with hydrophilic ionic liquid[a].

$[AlkylGBOEt^+][Br^-]$[b] (mol L^{-1})	% Au removed (E_{Au})		
	$[EtGBOEt^+][Br^-]$	$[PrGBOEt^+]$-$[Br^-]$	$[BuGBOEt^+]$-$[Br^-]$
4×10^{-3}	99.8	94.7	96.2
8×10^{-3}	99.9	99.8	97.2
2×10^{-2}	99.9	99.9	95.3
4×10^{-2}	99.9	99.9	97.1

[a] The concentration values of $[AlkylGBOEt^+][Br^-]$ are those after the mixing of gold(III) and bromide salt solutions ; [Au(III)] = 4×10^{-3} mol L^{-1}; [b] Alkyl = ethyl, *n*-propyl or *n*-butyl].

To obtain direct information of the interaction between $[AlkylGBOEt^+]$ and $[AuX_4^-]$, the IR spectra of precipitates were carried out. The presence of $[AlkylGBOEt^+]$ cation in the precipitate was confirmed by the presence of aliphatic C-H stretch (2989, 2938 (Alkyl = C_2H_5) 2980, 2920 (Alkyl = *n*-C_3H_7) and 2961, 2873 (Alkyl = *n*-C_4H_9) and C=O stretch (1741, 1620 (Alkyl = C_2H_5) 1736, 1629 (Alkyl = *n*-C_3H_7) and 1740, 1622 (Alkyl = *n*-C_4H_9). The carbonyl vibrations in $[AlkylGBOEt^+][AuX_4^-]$ are only slightly shifted, compared to those of the corresponding bromide salts which crystallize with one water molecule. This means that the interaction of the organic cations and AuX_4^- is mainly of electrostatic nature and the association is less soluble than the corresponding bromide salt of organic cations . In $[AlkylGBOEt^+][AuX_4^-]$, the O-H stretch present in the IR spectrum of the bromide salt, is attenuated because of the lesser hydrophilicity of these complexes.

The E_{Au} values first reveal that gold is successfully removed from water using hydrophilic bromide salt of $[AlkylGBOEt^+]$ cations. Starting with an aqueous gold solution of 8×10^{-3} mol L^{-1}, the values of E_{Au} exceed 95%. The extraction efficiency is comparable, whatever the salt used, and seems not to be related to the length of alkyl groups.

Liquid-liquid extraction of AuX_4^-

The values of the extraction percentage (E) and of the distribution coefficient (D) for $AuCl_4^-$ and $AuBr_4^-$ with $[BuGBOEt^+][Tf_2N^-]$ and $[EtGBOEt^+][Tf_2N^-]$ ILs are given in Table 3. Snapshots of the extraction of AuX_4^- are depicted in figure 4.

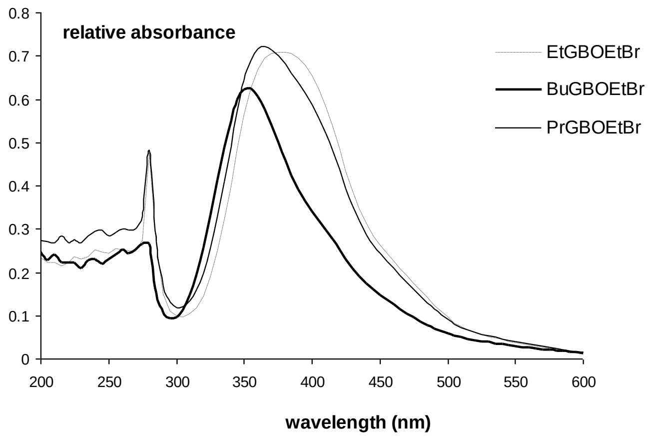

Figure 3: UV-vis spectra of $[AlkylGBOEt^+][AuX_4^-]$ precipitates dissolved in ethyl-acetate

After contacting $[EtGBOEt^+][Tf_2N^-]$, $[BuGBOEt^+][Tf_2N^-]$ and $[BuGBOEt^+][Dca^-]$ with $HAuCl_4$ solution, the ionic liquid phase turned yellow (orange in the case of $AuBr_4^-$). All the values of extraction yield, reported in the Table 3, exceed 95%, whatever the concentration used, revealing that gold is extracted efficiently from water. As expected, the D values indicate that $AuBr_4^-$ has more affinity for ionic liquid phase than $AuCl_4^-$, in accordance with the relative K_{Au} values (Table 1), which measure the affinity of tetrahalogenoaurate anion for the organic cations. In a similar way, the stronger affinity of tetrahalogenoaurate anions for $[BuGBOEt^+][Tf_2N^-]$ compared to that for $[EtGBOEt^+][Tf_2N^-]$, as evidenced by the D values (table 1), is in connection with the highest K_{Au} values determined for $[BuGBOEt^+][AuX_4^-]$.

Table 3 : Extraction efficiency of gold complexes (%E) in water with hydrophobic ionic liquid, the corresponding values of distribution coefficient are indicated in bracket.

	$C_{Au(III)}$ (mol L^{-1})	% Au extracted (%E)		
		$[EtGBOEt^+][Tf_2N^-]$	$[BuGBOEt^+][Tf_2N^-]$	$[BuGBOEt^+][Dca^-]$
$AuCl_4^-$	4×10^{-3}	99.9 (260)	97.1 (350)	-
	6×10^{-3}	99.9 (116)	99.9 (282)	-
	8×10^{-3}	99.9	99.9	99.9 (>500)
$AuBr_4^-$	4×10^{-3}	99.9	99.9	
	8×10^{-3}	99.9	99.1	

Moreover, the D values evidence a stronger affinity of tetrahalogenoaurate ions for $[BuGBOEt^+][Dca^-]$ than for $[BuGBOEt^+][Tf_2N^-]$. Such a trend can be explained by the higher hydrophilicity of dicyanamide anion that may enhance anionic exchange with AuX_4^- and consequently, the extraction yield.

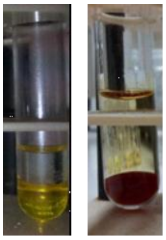

Figure 4 : Snapshot of ionic liquid phases after extraction of $AuCl_4^-$ (left) and $AuBr_4^-$ anions (right).

Mechanism of extraction

It is generally assumed, that the transfer of anionic complexes such as AuX_4^- from aqueous to IL phase proceeds either by ion-pairing or by anionic exchange[12-15,22-24]. Ion pairing and anionic exchange are described by the equilibria (4) and (5) :

Ion-pairing (IP) :

$$AuX_4^-{}_{(w)} + C^+{}_{(w)} \rightleftharpoons C^+{}_{(IL)} + AuX_4^-{}_{(IL)} \qquad (4)$$

Anionic exchange (AE) :

$$AuX_4^-{}_{(w)} + A^-{}_{(IL)} \rightleftharpoons AuX_4^-{}_{(IL)} + A^-{}_{(w)} \qquad (5)$$

In general case, the related equilibria constants for the ion pair extraction and the ion exchange reaction are expressed by eqs (6) and (7), respectively.

$$K_{IP\text{-}ex} = [AuX_4^-]_{IL}/[AuX_4^-]_w[C^+]_w \qquad (6)$$

$$K_{AE\text{-}ex} = [AuX_4^-]_{IL}[A^-]_w/[AuX_4^-]_w \qquad (7)$$

These equations are based on the assumption of dilute solutions. Therefore, it is assumed that the activities of C^+ and A^- in the ionic liquid phase are equal to unity, and that no aggregates or micelles are formed.

The anionic exchange and the ion-pairing extraction are connected (or concerted) processes that may occur simultaneously. These processes are interrelated by the solubility product of ionic liquid that defines the relationship between the cation and the anion of ionic liquid in the aqueous phase. The eqs. 8 and 9 are the equilibrium and the mass action law for ionic liquid in contact with an aqueous phase.[25]

$$C^+{}_{IL} + A^-{}_{IL} \rightleftharpoons C^+{}_w + A^-{}_w \qquad (8)$$

$$K_{sp} = [C^+][A^-] = s^2 \qquad (9)$$

where s is the ionic liquid solubility in water and K_{sp}, the solubility product of ILs. In both cases the subscripts "IL" and "w" indicate a species present in the IL and aqueous phases, respectively. In water, the solubility of $[EtGBOEt^+][Tf_2N^-]$ $[BuGBOEt^+][Tf_2N^-]$ and $[BuGBOEt^+][Dca^-]$ are 1.46×10^{-3}, 1.88×10^{-2} and 1.80×10^{-1} mol L^{-1}, respectively and their corresponding solubility products are 2.13×10^{-6}, 3.53×10^{-4} and 3.24×10^{-2}, respectively. Before extraction the concentration of C^+ and A^- are equivalent. The ionic liquid phases can be considered as infinite reservoirs of their individual components, whatever the process involved for the extraction of AuX_4^-. After extraction, the concentrations of the organic cation and the anion in aqueous phase, should verify the solubility product of ionic liquid. For example, if the overall extraction process involves only ion-pairing mechanism, the consumption of organic cations due to the formation and solubilisation of $[C^+][AuX_4^-]$ in ionic liquid phase should be compensated by an increase of the concentration of $[A^-]$ in aqueous solution. Inversely, a pure anionic exchange mechanism induces an increase of the $[A^-]$ concentration in aqueous solution that should be compensated by a decrease of the concentration of organic cation in water. These considerations render difficult the discrimination between ion-pairing mechanism and anionic exchange. Nevertheless, with $[EtGBOEt^+][Tf_2N^-]$ and $[BuGBOEt^+][Tf_2N^-]$, it is possible to determine which mechanism operates or prevails from the analysis of sulphur release in aqueous solution which accompanies, the transfer of AuX_4^- from the aqueous to the ionic liquid phase. If we assume a pure ion-pairing process, the concentration of $[AlkylGBOEt^+]$ in water can be estimated from the extraction yield of AuX_4^- (E_{Au}):

$$[AlkylGBOEt^+]_{IP} = s - C_{AuX_4^-} \times E_{Au} \qquad (10)$$

Since the concentrations of $[AlkylGBOEt^+]$ and $[Tf_2N^-]$, in the presence of AuX_4^-, should check the solubility products of $[AlkylGBOEt^+][Tf_2N^-]$, the concentrations of Tf_2N^- in the aqueous phase can be calculated from the following equation :

$$[Tf_2N^-]_{IP} = \frac{K_{sp}}{[AlkylGBOEt^+]} = \frac{K_{sp}}{s-(C_{AuX_4^-} * E_{Au})} \qquad (11)$$

Inversely in a case of a pure anionic exchange process the concentration of $[Tf_2N^-]$ in water is estimated from the extraction yield of AuX_4^- :

$$[Tf_2N^-]_{AE} = s + C_{AuX_4^-} * E_{Au} \qquad (12)$$

$$[AlkylGBOEt^+]_{AE} = \frac{K_{sp}}{[Tf_2N^-]} = \frac{K_{sp}}{s+(C_{AuX_4^-} * E_{Au})} \qquad (13)$$

It is clearly seen, that the concentration of $[Tf_2N^-]$ in aqueous solution will be different according to the type of mechanism involved in the transfer of AuX_4^-. The determination of sulphur content in aqueous solution makes it possible to estimate that of Tf_2N^- after extraction. Then it is possible to identify the mechanism involved in the transfer of AuX_4^- from aqueous solution to IL phase. Figure 5 shows experimental and calculated concentrations of Tf_2N^- in aqueous solution for anionic exchange or ion-pairing mechanisms, with $[BuGBOEt^+][Tf_2N^-]$ and $[EtGBOEt^+][Tf_2N^-]$, and for several concentrations of $HAuCl_4$. Similar trends are observed with the $AuBr_4^-$ ions for both ionic liquids.

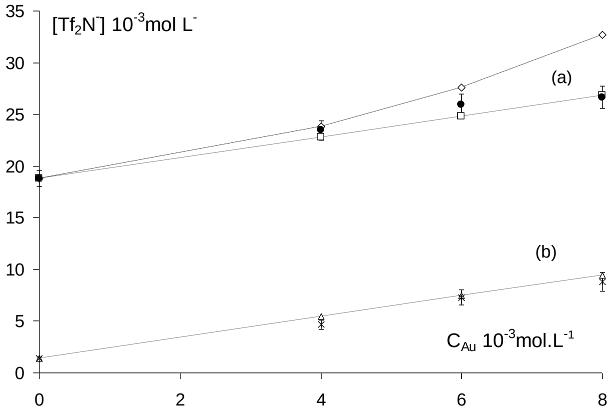

Figure 5 : Release of Tf_2N^- in aqueous solution after extraction of $AuCl_4^-$ in (a) $[EtGBOEt^+][Tf_2N^-]$ IL and (b) $[BuGBOEt^+][Tf_2N^-]$ IL as a function of $AuCl_4^-$ initial concentration

(●) experimental data (☐) calculated from eq.11 considering anionic-exchange mechanism (◇) calculated from eq. 10 considering ion-pairing extraction mode for $[EtGBOEt^+][Tf_2N^-]$–$HAuCl_4$ system ;

(∗) experimental data (Δ) calculated from eq. 12 considering anionic-exchange mechanism for $[BuGBOEt^+][Tf_2N^-]$ – $HAuCl_4$ system

The solubility of $[BuGBOEt^+][Tf_2N^-]$ is lesser than the concentrations of $AuCl_4^-$ used in our experiments, so that a pure ion-pairing process can not be considered. In this case, it is not possible to calculate the release of sulphur in water associated to this process.

Moreover, as seen in figure 5, with $[BuGBOEt^+][Tf_2N^-]$, whatever the initial concentration of $AuCl_4^-$, the experimental concentrations of $[Tf_2N^-]_{exp}$ are really close to those calculated with a pure anion exchange mechanism meaning that this process prevails in this system. It is interesting to note that the calculations of the Tf_2N^- release in aqueous solution, carried out by considering a mixed process, anion exchange and ion pairing, would lead to higher values of Tf_2N^- release than those calculated with a pure ion exchange process.

The extraction mode with $[EtGBOEt^+][Tf_2N^-]$ involves simultaneously a mixed process by ion pairing and anionic exchange (figure 5), for concentrations of AuX_4^- lower than 6×10^{-3} mol L^{-1}. However, we observe a gradual increase of AuX_4^- extraction by anionic exchange with the increase of the $AuCl_4^-$ concentration in solution. The extraction of AuX_4^- for a concentration of 8×10^{-3} mol L^{-1} proceeds at 95% *via* anionic exchange. The higher rate of AuX_4^- extraction *via* ion-pairing for $[EtGBOEt^+][Tf_2N^-]$ compared to $[BuGBOEt^+][Tf_2N^-]$ is related to its higher solubility which leads to a greater concentration of organic cation in solution, enhancing the formation of ion-pairs in aqueous solution.

To further confirm the validity of anionic exchange and ion-pairing mechanism, for the partitioning of AuX_4^- between water and the IL phases, extraction experiments were carried out with $LiTf_2N$ solutions at concentrations ranging between 0.05 and 0.5 mol L^{-1}. These experiments allow us to examine the influence of Tf_2N^- concentration in aqueous solution on the distribution coefficient of gold between aqueous and the IL phases. Similar extraction experiments of tetrahalogenoaurate anions in NaDca aqueous solutions, with concentrations ranging between 0.2 and 1 mol L^{-1}, are carried out using $[BuGBOEt^+][Dca^-]$ as extractant phase. Considering the mass action law relative to anionic exchange (eqs. 5 and 7), the distribution coefficient of AuX_4^- should decrease with the increase of the $[A^-]$ concentration in aqueous solution. This is confirmed by experimental results (figure 6), which show a drastic effect of the increase of the anion concentration, in aqueous phase, on the coefficient distribution values. This indicates that the anions constitutive of ILs compete with tetrahalogenoaurate anions in metathesis reactions with organic cations. This result confirms the predominance of the anionic exchange as a main extraction mode for all the studied systems.

The equilibrium constants associated to anionic exchange and ion-pairing transfer of tetrahalogenoraurate anions from aqueous to IL phase (eqs. 6 and 7) were determined by the approach developed by Katsuta *et al.* [25, 26]

According to the mass action laws (eqs. 6 and 7), the distribution coefficient are related to the concentrations of $[A^-]_w$ and $[C^+]_w$, by the following equations :

$$\log D = \log K_{IP\text{-}ex} + \log[C^+]_w \qquad (14)$$

$$\log D = \log K_{AE\text{-}ex} - \log[A^-]_w \qquad (15)$$

Therefore $K_{IP\text{-}ex}$ and $K_{AE\text{-}ex}$ are related by the relation:

$$K_{AE\text{-}ex}/ K_{IP\text{-}ex} = K_{sp} \qquad (16)$$

The equilibrium constants of eqs. 6 and 7 can be determined from eq. 15, by plotting $\log D_{Au}$ as a function of the logarithm of the anion concentration log $[A^-]$ (figure 7). The slope of the graph should be equal to unity and the intercept gives the $K_{AE\text{-}ex}$ value. Then the $K_{IP\text{-}ex}$ value can be deduced from the value of $K_{AE\text{-}ex}$ and the solubility product of ionic liquid K_{sp}. In our fitting procedure, a slope equal to unity was imposed. For the Tf_2N^- based ILs, the Katsuta model fits quite well the experimental data (figure 7) obtained with $AuBr_4^-$, with good correlation coefficients (r^2 >0.98). The applicability of Katsuta's model remain acceptable, in the case of $AuCl_4^-$, but with less good correlation coefficients ($r^2 \geq 0.93$).

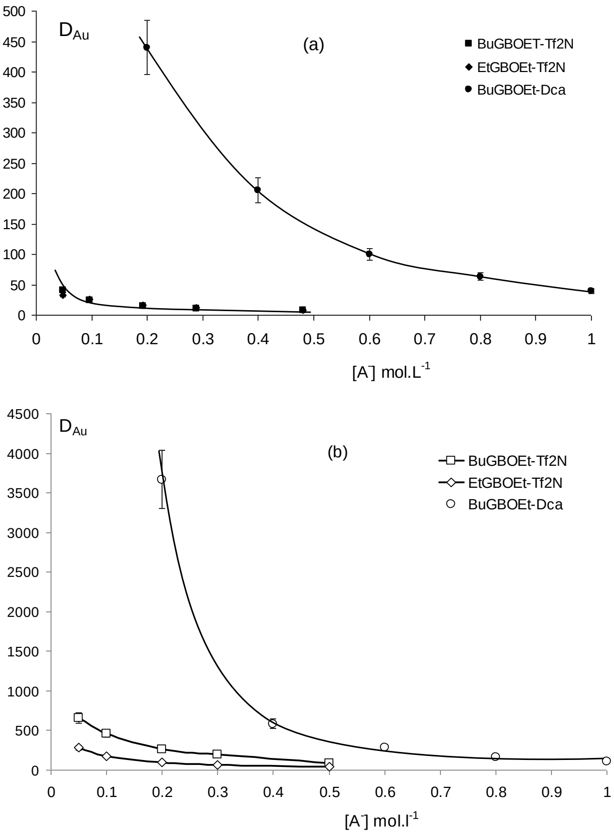

Figure 6 : The distribution ratio (D) of AuX_4^- as a function of the concentration of the anion $[A^-]$ (a) $AuCl_4^-$, (results obtained with $[BuGBOEt^+][Tf_2N^-]$ and $[EtGBOEt^+][Tf_2N^-]$ ILs are very close and, for clarity only one curve was depicted in the graph to represent the general trend observed), (b) $AuBr_4^-$

The least applicability of the Katsuta's model to the experimental data obtained with $AuCl_4^-$ may be related to the lower stability of this anion in aqueous solution. Indeed, Au-Br bonds are more stable than that of Au-Cl, and $AuBr_4^-$ is more resistant to hydrolysis, or even to reduction processes, than $AuCl_4^-$. For $[BuGBOEt^+][Dca^-]$, the applicability of Katsuta's model is poor, since larger deviations from unity were determined for slopes of logD versus log$[A^-]$ plot. As shown in the following section, such a result is imputable to a partial substitution of halogen ions by dicyanamide which occurs for high concentration of NaDca. The $K_{AE\text{-}ex}$ and $K_{IP\text{-}ex}$ values for $AuCl_4^-$ and $AuBr_4^-$ were nevertheless determined for all system, since they can provide qualitative and comparative insights on the factors governing the partitioning of AuX_4^- between aqueous and ionic liquid phases. All the values of $K_{AE\text{-}ex}$ and $K_{IP\text{-}ex}$ and K_{sp} values are reported in table 4. The magnitude of $K_{IP\text{-}ex}$ values follows those of the K_{Au} values, meaning that the partitioning of tetrahalogenoaurate anion between the aqueous and ionic liquid phases is strongly dependent on the intrinsic affinity of the tetrahalogenoaurate anion for the cation of the ionic liquid. Indeed, the D_{Au} values are higher for $AuBr_4^-$ than for $AuCl_4^-$, like those obtained with

$[BuGBOEt^+][Tf_2N^-]$ compared to $[EtGBOEt^+][Tf_2N^-]$. Moreover, it appears clearly that partitioning is also dependent on the hydrophilic/hydrophobic character of the anion of the ionic liquid. A hydrophilic anion will be exchanged more easily with tetrahalogenoaurate anion than an hydrophobic anion. The relative values of K_{AE-ex} are compatible with the fact that Dca^- anion is more hydrophilic than Tf_2N^- anion and consequently the D_{Au} values are higher with Dca^- based ILs than with Tf_2N^- based ILs.

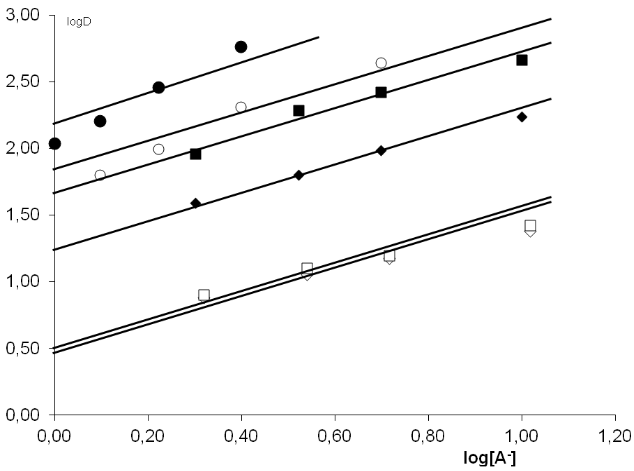

Figure 7 : Plot of $logD_{Au}$ versus log $[A^-]$ concentration, open symbol $AuCl_4^-$ filled symbol $AuBr_4^-$ (◆)$[EtGBOEt^+][Tf_2N^-]$ (■)$[BuGBOEt^+][Tf_2N^-]$ (●)$[BuGBOEt^+][Dca^-]$.

Table 4 : the K_{IE-ex} and K_{IP-ex} values determined from figure 7, by application of Katsuta's model.

ILs	Anion	K_{IE-ex}	K_{IP-ex}
$[EtGBOEt^+][Tf_2N^-]$	$AuCl_4^-$	2.76	$7.82\times10^{+3}$
$[BuGBOEt^+][Tf_2N^-]$	$AuCl_4^-$	2.52	$1.18\times10^{+6}$
$[BuGBOEt^+][Dca^-]$	$AuCl_4^-$	83.20	$3.91\times10^{+7}$
$[EtGBOEt^+][Tf_2N^-]$	$AuBr_4^-$	17.93	$5.08\times10^{+4}$
$[BuGBOEt^+][Tf_2N^-]$	$AuBr_4^-$	48.31	$2.27\times10^{+7}$
$[BuGBOEt^+][Dca^-]$	$AuBr_4^-$	194.3	$9.12\times10^{+7}$

We analyzed the coordination of Au(III) in aqueous solution and in ILs phase, dissolved in ethyl-acetate, by UV-vis spectroscopies. The figure 8 shows $AuCl_4^-$ and $AuBr_4^-$ absorption spectra in water and in ILs phases. The absorption spectra of gold complexes in IL phases, with $[EtGBOEt^+][Tf_2N^-]$ and $[BuGBOEt^+][Tf_2N^-]$ ILs, show similar features as those in aqueous solutions, regardless of the concentration of AuX_4^- extracted. These observations indicate that the coordination of Au(III) does not change and that the ILs phases contain the $AuCl_4^-$ or$AuBr_4^-$ species. The absorption maximum appears at 323 nm in $[BuGBOEt^+][Tf_2N^-]$ phase and at 333 nm in $[EtGBOEt^+][Tf_2N^-]$ for $AuCl_4^-$ species. The peak shifting may be caused by the interaction between organic cation with AuX_4^- or by the change of solvent (ethyl acetate). A similar trend is observed with $AuBr_4^-$ with a shift of the absorbance maximum close to 20 nm. The UV-vis spectra of the two tetrahalogenoaurate anion, in $[BuGBOEt^+][Dca^-]$, present nearly the same feature with a sharp transition between 250-260 nm and a shoulder between 270-280 nm. As seen earlier, such a shift towards higher energy compared to the spectrum in aqueous media or in Tf_2N^- based ionic liquid, can be ascribed to the substitution of bromide or chloride ion by dicyanamide anion. This interpretation was confirmed by a titration of $HAuCl_4$ and $HAuBr_4$ ion by NaDca in aqueous solutions (results not shown here). The substitution is effective for ratio $[Dca^-]/[AuX_4^-]$ higher than 200, this condition is reached in $[BuGBOEt^+][Dca^-]$ where the Dca^- concentration is estimated close to 3 mol L^{-1}, the concentration of AuX_4^- used in all our experiments being less than $1x10^{-2}$ mol L^{-1}.

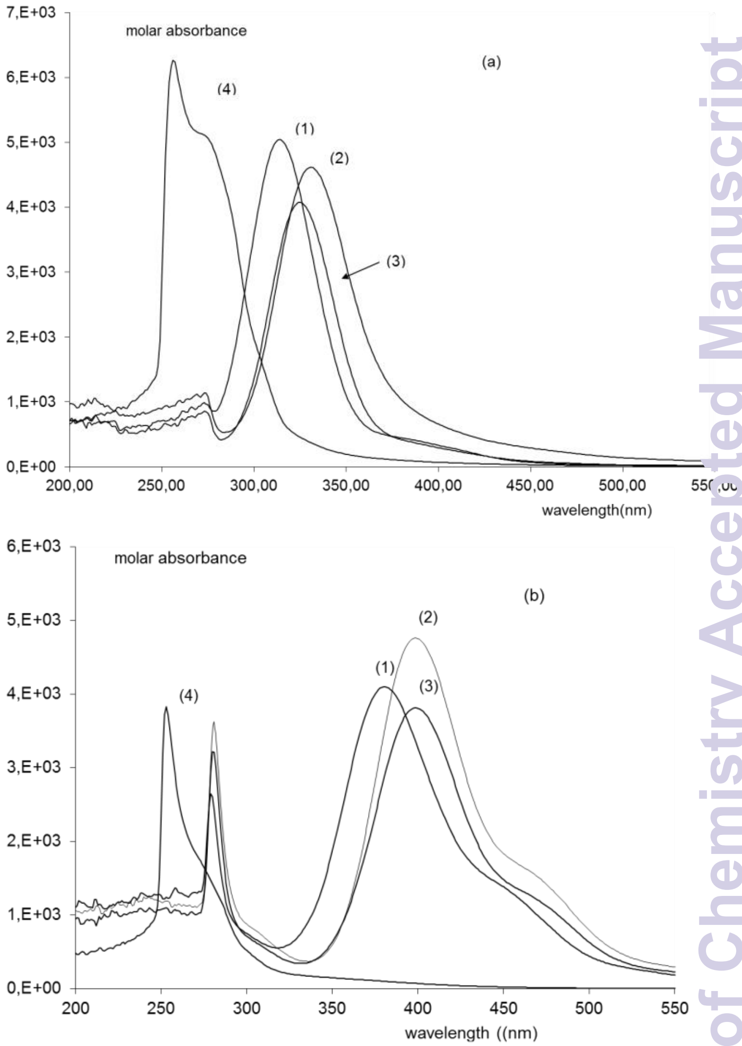

Figure 8 : UV-vis spectra of tetrahalogenoaurate anions in ionic liquid phase (a) $AuCl_4^-$ (b) $AuBr_4^-$: (1) aqueous solution, (2) $[EtGBOEt^+][Tf_2N^-]$, (3) $[BuGBOEt^+][Tf_2N^-]$ (4) $[BuGBOEt^+][Dca^-]$.

Conclusion

Tetrahalogenoaurate anions have been successfully removed from water using betaine derivative cations ILs. Such compounds, which are accessible *via* simple synthetic routes, may constitute good substitutes to the organic solvents and allow the development of proper methodology for the gold recovery from aqueous industrial effluents. Anionic gold complexes may be efficiently extracted from water by using hydrophilic bromide salt of betaine derivative. In all cases gold is removed very efficiently from the aqueous phase with an extraction yield higher than 90%. The liquid-liquid extraction of gold(III) carried out with hydrophobic ionic liquids, constituted by the association of cationic betaine derivatives with bis(trifluoromethanesulfonyl)imide (Tf_2N^-) or dicyanamide anions (Dca^-), leads to the extraction yields and the distribution coefficients higher than 99% and 150, respectively. The affinity of tetrahalogenoaurate anions for the IL phases increases in the order :

$$[EtGBOEt^+][Tf_2N^-] < [BuGBOEt^+][Tf_2N^-] < [BuGBOEt^+][Dca^-]$$

And the affinity of tetrahalogenoaurate anions for the ionic liquid phases increases in the order :

$$[AuCl_4^-] < [AuBr_4^-]$$

These trends are in accordance with the strength of the interaction between tetrahalogenoaurate anions and organic cation evaluated by the determination of the K_{Au} values. However, the higher affinity of tetrahalogenoaurate anions for dicyanamide based ILs, compared to bis(trifluoromethanesulfonyl)imide one, can be explained by the higher hydrophilicity of dicyanamide anion which favors anionic exchange process.

Experimental

Reagents

$HAuCl_4$,$3H_2O$ (99.9%) was purchased from Aldrich**.** For extraction experiments, a stock solution was prepared with highly purified water and metal salts. The solutions of $AuBr_4^-$ were prepared from $HAuCl_4$ solutions by addition of sodium bromide in a ratio $[Br^-]/[Au(III)]$ equal to 10. The complete conversion of $AuCl_4^-$ into $AuBr_4^-$ was checked by UV-vis spectrophotometry.

Precipitation experiments

The precipitation experiments are carried out by mixing 1.5 mL of the initial solution of $HAuCl_4$ at a concentration of 8×10^{-3} mol L^{-1}, with 1.5 mL of $[AlkylGBOEt^+][Br^-]$ at concentrations ranging between 8 10^{-3} and 8 10^{-2} mol L^{-1}. For each experiment, the tube was placed on a shaker for 24h and then centrifuged at 2000 rpm for 10 minutes. The residual concentration of $AuCl_4^-$ in aqueous solution was determined by UV-vis spectroscopy. The same experiments were carried out with $AuBr_4^-$ to determine the solubility product of $[EtGBOEt^+][AuBr_4^-]$, $[PrGBOEt^+][AuBr_4^-]$ and $[BuGBOEt^+][AuBr_4^-]$. Since $AuCl_4^-$ based ionic liquids were more soluble than their analog compounds containing $AuBr_4^-$, the solubility product of $[EtGBOEt^+][AuCl_4^-]$, $[PrGBOEt^+][AuCl_4^-]$ and $[BuGBOEt^+][AuCl_4^-]$ were determined by contacting $HAuCl_4$ solutions with aqueous solutions saturated by $[BuGBOEt^+][Tf_2N^-]$ and $[EtGBOEt^+][Tf_2N^-]$. In this case, to avoid dilution of aqueous saturated ILs solutions by $AuCl_4^-$ solutions, 2 mL of aqueous solution previously contacted during 24 hours with ILs phase, was collected and lyophilized. The lyophilisat of aqueous phase was then contacted with 2 mL $AuCl_4^-$ solution. Thus no dilution occurs upon mixing of the IL and the $AuCl_4^-$ solutions, and the conditions for the precipitation of $[AlkylGBOEt^+][AuCl_4^-]$ are reached. The solutions were then shaken during 24 hours and centrifugated before analysis. The initial concentration of organic cation was determined from the measurements of sulphur concentration by ICP-OES spectroscopy. It was previously checked, by sulphur and TOC measurements, that the lyophilisation does not affect the composition of aqueous solutions.

Extraction experiments

Au(III) aqueous solutions were prepared by dissolution of $HAuCl_4$, $3H_2O$ in deionized water. Extraction yields (E) and distribution ratios (D) were determined by mixing equal volume (1 mL) of IL and aqueous phase. The mixture was shaken for 24h to reach equilibrium and then centrifugated at 2000 rpm during 5 minutes. The phases were then separated for analysis. The Au(III) content metal ion in the aqueous phase was determined by UV-vis spectroscopies applying the Beer–Lambert law at the maximum absorption wavelength ($\lambda_{max} \approx 313$ nm and 380 nm for $AuCl_4^-$ and $AuBr_4^-$, respectively) of gold complexes and using calibration solutions ranging from 10 to 100µmol L^{-1}. Before analysis, the samples were diluted in HCl or HBr 0.05 mol L^{-1} to suppress hydrolysis of solutions before analysis. According to Usher *et al.*[21] $AlCl_4^-$ is stable below pH 3 and $AuBr_4^-$below pH 4. Moreover, in the case of $AuCl_4^-$, a calculation based on the dissociation constant of $AuCl_4$- and $AuCl_3OH^-$ determined by Wagman et al.[27] and Baes and Mesmer[28], show that in our conditions, the extent of hydrolysis does not exceed 1%.

Complementary measurements were monitored by ICP-OES from Thermoscientific (cap 6000 series) to confirm the UV-vis measurements. In all cases, the pH of aqueous phase was checked before and after gold extraction. Since solutions are not buffered, the pH was related to the free concentration of H^+ ions brought by $HAuCl_4$, $3H_2O$. The pH variations during the extraction process were negligible. The metal ion concentration in the IL phase was deduced from the difference between the initial concentration of metal ion in the aqueous phase and the concentration of metal ion after extraction.

The efficiency of the extraction process was evaluated by the determination of the extraction percentage (%E) calculated using the following equation:

$$\%E = 100 * \frac{(C_{in} - C_{fin})}{C_{in}} \frac{V_w}{V_{IL}} \quad (17)$$

where C_{in} and C_{fin} (mol L^{-1}) represent the concentrations in the initial and in the final aqueous solution, respectively. V_w and V_{IL} correspond to the volumes of water and ionic liquid, respectively; in general, V_w and V_{IL} are equal to 1 mL. However, for the analysis of the extraction mode of AuX_4^-, some experiments were done with a ratio V_w/V_{IL} equal to 4. The extraction percentages (%E) were determined at 298 K. The concentration of Au(III) solutions lies in the range from 4×10^{-3} to 8×10^{-3} mol L^{-1}. The experimental error on the extraction yield values is estimated to be less than 3%.

For the liquid–liquid extraction experiments, the distribution coefficient (D) is calculated using the following formula.

$$D = \frac{(C_{in} - C_{fin})}{C_{fin}} \frac{V_w}{V_{IL}} \quad (18)$$

The maximum D value measurable in this study is assumed to be 5×10^2. The relative uncertainty on D is ± 10%. Experimental results, done in duplicate, agree within 5%.

Physical measurements

Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 2400 C, H, N element analyzer in our University. UV-visible spectra of Au(III) solutions were recorded using a Carry-5000 Varian spectrophotometer. Total concentration of sulphur and gold were carried out by ICP-OES from Thermoscientific (cap 6000 series).

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