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Speciation and quantitation of precious metals in model acidic leach liquors, theoretical and practical aspects of recycling

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Abstract

Waste printed circuit boards are a major source of strategic materials such as platinum group metals since they are used for the fabrication of technological devices, such as hard drive discs, capacitors, diodes, etc. Because of the high cost of platinum, palladium and gold (> 25k€ / kg), an economic and environmental challenge is their recycling from printed circuit boards, that represent around 2% weight of electronic equipment. Hydrometallurgical treatments allow to recover these metals in solution, with a high recovery rate for a leaching liquor made of thiourea in hydrochloric acid. So as to develop an efficient recycling process from this leach liquor, one requires the speciation of these strategic metals, as well as their extraction and quantitation in the mixture. For this purpose, platinum, palladium and gold were dissolved in model leach liquors made of hydrochloric acid and thiourea at low concentration. The identification of metal complexes was determined in function of thiourea concentration (between 10 µmol/L and 10 mmol/L) by the combination of UV-Visible spectrometry, cyclic voltammetry and for the first time capillary electrophoresis. The electrokinetic method was then applied for the quantitation of trace metal analyses in leach samples from waste printed circuit boards reprocessing, demonstrating its applicability for industrializable recycling applications.

24 **Keywords**

25 Strategic metals –Thiourea – UV spectrophotometry – Voltammetry – Electrophoresis

26 **Declarations**

27 Not Applicable

Introduction

The Electrical and Electronic Equipment (EEE) are more and more common in our daily life, and their production is still increasing since the past decades. Computers, smartphones or televisions represent a major source of diverse materials such as strategic ones, as they turn to become waste (WEEE, Waste Electrical and Electronic Equipment). Those materials are defined by the European Commission [1] as species with supply risks and of high economic issue. Particularly, the Printed Circuits Boards (PCBs) - that compose almost 2% weight of the WEEE [2] - contain a high diversity of strategic materials, like platinum group metals (PGM) or rare earth elements. These elements that are mostly produced in South Africa and in Russia [3] are present in relatively low content (< 1% weight) but represent a high added value that needs to be valorized because of their nature (Fig. S1).

Particularly, platinum (Pt) and palladium (Pd) are used in the fabrication process of hard drive discs, capacitors, diodes, etc. Pt and Pd recovery is even more interesting due to their high cost (>25 k€ per kilogram in 2018) [4]. Gold (Au), which is not currently considered as critical raw material, is also interesting to collect because it represents the most recoverable metallic species in PCBs. It has to be taken into account that the spatial and temporal origin of a PCBs is of importance, due to the fact that the EEE are becoming more and more efficient since the last decades and tend to contain more and more critical materials.

The recycling process of the waste PCBs is an important step for the recovery of these metals, and goes through different steps described in the literature that can be summarized as follows [5] : (i) a mechanical treatment to split different categories of materials (plastics, ferrous and non-ferrous metals), (ii) pyrolysis technics to remove plastics that remain in order to obtain a metallic powder, and (iii) hydrometallurgical treatments to dissolve the metals (selectively or not) by leaching. There exists a lot of different media to perform the leaching of Pt, Pd and Au, such as acidic aqueous media containing oxidizing agents, cyanide or other organic ligands (thiourea, thiosulfate...). Depending on the composition of the leach liquor, the selectivity and the kinetics of dissolution reaction of the metallic compounds vary from one method to another (Table S1).

Hydrochloric acid (HCl) leaching has shown great results, with a good efficiency in particular for precious metals, such as Au and Pd. With an efficiency that can reach 100%, the use of concentrated aqueous HCl solution (from 0.1 to 5 mol/L) containing Cl_2 , H_2O_2 or NaClO_4 is useful to selectively remove precious metals from waste PCBs, even

if other metallic species such as copper are noticed to be also leached and thus interfering in the recycling process. But this treatment in general doesn't stop at this point. Subsequent purification steps can be involved.

The leach liquor is treated to be cleaned from what can be considered as lowering the performances of the process (such as other ions, plastics, etc...). In the case of waste PCBs, and due to its mean composition, copper and other common metals like iron and tin can also be found in the leach liquor. Several methods were developed for the purification of PCBs leach liquor, such as liquid-liquid extraction [6], the use of exchange resin [7], precipitation [8] and cementation [9]. The chemical modification of resin with thiourea has shown great results concerning the retention of some of the above cited species. Indeed, thiourea has been used for the modification of different support, such as magnetic nanoparticles [10] or chitosan [11] and shows strong interaction with precious metal ions. Thiourea is also used for the elution of these species from some commercial resins dedicated to the specific retention of precious metals in acidic media [12], forming new complexes in concentrated and purified solution. The purification process with thiourea-based sorbent or by elution containing thiourea is thus promising and of interest for the specific recovery of PGM, since it allows a good selectivity. In this context, the speciation of these metals in leach liquors is of interest to fully understand their behaviour, to optimize the hydrometallurgical treatment and the recovery process.

For now, some studies focused on precious metals complexation with thiourea, showing a different behavior of each metal in acidic media (sulfuric acid, HCl and nitric acid). For example, Au(III) is spontaneously reduced to its Au(I) form, interacting with thiourea in excess to form one single complex of $\text{Au}(\text{thiourea})_2^+$ [13]. In the case of Pd, chloride ions from PdCl_4^{2-} can be replaced by thiourea, to form consequently $\text{Pd}(\text{thiourea})_4^{2+}$, with intermediates such as, $\text{PdCl}_2(\text{thiourea})_2$ and $\text{Pd}_2(\text{thiourea})_2\text{Cl}_4$ [14, 15]. For the Pt ion, the rare studies devoted to the analysis of the exact mechanism of complexation with thiourea assume that Pt(IV) is reduced to Pt(II) to form $\text{Pt}(\text{thiourea})_4^{2+}$, or to form dimer complexes [16].

In order to complete the knowledge about the speciation of Pt, Pd and Au ions in acidic solution in terms of complexation and oxidation states, UV-visible spectrophotometry, capillary electrophoresis (CE) and voltammetry have been used for the analysis of these metal ions in artificial leach liquor, in the absence or presence of thiourea at different concentrations, and the understanding of interaction mechanisms is discussed. The performance of capillary electrophoresis for thiourea-complexes detection and quantitation is then demonstrated by analysing real leach

liquors, spiked with known quantities of precious metals and pretreated on solid phase extractant dedicated to the specific recovery of platinum group metals and precious metals (Pt, Pd, Au...).

Material and Methods

Reagent

The artificial leach liquors were made by dilution of appropriate amounts of standard solution of Gold Standard for ICP TraceCERT® 1000 mg/L (5% HCl, Sigma-Aldrich co. LCC., Paris, France), Palladium Standard for ICP TraceCERT® 10000 mg/L and Platinum Standard for ICP TraceCERT® 10000 mg/L (10% HCl with HNO₃- traces, Sigma-Aldrich co. LCC, Paris, France) in 1 mol/L HCl (made from HCl for analysis 37%. Acros Organics, Geel, Belgium) and Ultrapure water. CuCl₂ (99%), Thiourea (ACS reagent, ≥99.0%) and NaCl (BioXtra. ≥99.5%) were provided by Sigma-Aldrich (Paris, France).

UV-Visible spectrophotometry

UV/Vis absorption spectra were acquired on a Lambda 750 UV/Vis/NIR Spectrophotometer (PerkinElmer Inc., Shelton, USA). The analyses were performed between 200 and 800 nm in a quartz cell. The solutions were diluted 50 times in 0.1 mol/L HCl prior to analysis to avoid signal saturation. 0.1 mol/L HCl was used as a blank solution.

Capillary electrophoresis

CE experiments were performed on an HP3DCE capillary electrophoresis system (Agilent Technologies. Waldbronn, Germany). The fused silica capillary dimensions (from Polymicro Technologies. Phoenix. AZ. USA) were 35 cm length, 50 µm intern diameter, with a detection window at 26.5 cm. The capillary activation was performed by flushing the capillary with 1 mol/L NaOH and 0.1 mol/L NaOH for 10 min, rinsed with water for 10 min, with 0.1mol/L HCl for 5 min and rinsed a second time with water for 5 min prior to analysis. The background electrolyte (BGE) was daily prepared, made of 1 mmol/L HCl and 50 mmol/L NaCl, without or with addition of thiourea (2 mmol/L) according to cases. Successive injections of sample and BGE were performed under 30 mbar for 2 s. The separation conditions were as follows: -11 kV for anions separation, +11 kV for cations separation; the diode array detector was used at different wavelengths. The temperature was maintained at 25°C for every experiment.

Electrochemistry

Cyclic and linear hydrodynamic voltammetry (CV and LHV) were performed in a classical three-electrode system cell, composed of glassy carbon (OrigaTip - Glassy Carbon Tip 3mm diameter, Origalys, Rillieux-la-Pape, France) used as working electrode (WE), a platinum wire as counter electrode (CE) and a Saturated Calomel Electrode (SCE, Radiometer Analytical) as reference electrode (RE). The acquisitions were performed with a Model 263A Potentiostat/Galvanostat (Princeton Applied Research, Oak Ridge, USA), coupled with the Powersuite software. LHV with rotating electrode at 1000 rpm were driven by an OrigaTrod Rotating Disk Electrode instrument (Origalys, Rillieux-la-Pape, France). All experiments were performed at room temperature ($T=23\pm2^{\circ}\text{C}$).

Leach liquor preparation and treatment

The preparation and process of PCBs leach liquor, either non spiked or spiked with a mixture of Pd and Au, at 10 mg/L each (named LL and LLsp, respectively) is described in fig. S2 and can be summarized as follow: 30 g of crushed waste PCBs ($< 750\text{ }\mu\text{m}$) [17] were immersed in 300 mL of a 1 mol/L HCl solution and 1.8 mL of a 30 % H_2O_2 (w/v, in water). The mixture was stirred at 500 rpm for 24 h prior to filtration on Whatman paper to remove particles. The filtered leach solution (referred to as solution LL_A) was then treated on a solid phase extraction cartridge (Analig® PM 07, GLSciences, Tokyo, Japan) [18–20] according to the following procedure: the cartridge was conditioned with 25 mL of a 1 mol/L HCl solution before loading 25 mL of LL_A . The sample matrix discarded through the loading step is called solution LL_B . The cartridge was then rinsed with 25 mL of a 1 mol/L HCl solution. Eventually, target analytes were desorbed and collected as three independent fractions referred to as solutions LL_{C1} , LL_{C2} and LL_{C3} respectively) originating from three successive elutions with 3.75 mL of a 0.5 mol/L thiourea solution in 0.1 mol/L HCl. Rinsing and elution steps were performed at a constant flow rate of 1 mL/min by applying a negative pressure with a peristaltic pump at the cartridge outlet. For controls, a 1 mol/L HCl solution, either pure or spiked with Pd and/or Au standard solutions (referred to as HCl and HClsp, respectively) and LLsp spiked with the same standard solutions to give a final concentration of 10 mg/L each were submitted to the same extraction process.

Results and discussion

In the present study, the different metallic ions (Pd, Pt and Au) are diluted in artificial acidic leach liquors, composed of HCl (concentration up to 0.1 mol/L) and thiourea, (concentration up to 10 mmol/L) at $\text{pH} = 1$. They are assumed

to complex with chloride ions and thiourea due to their high affinity binding ($\log K = 11.5$ and 30.1 with Pd(II) ,for chloride and thiourea respectively, at 25°C and 1 mol/L ionic strength [21], $\log K = 14.0$ for chloride with Pt(II) [21], and $\log K = 29.6$ for chloride with Au(III) [21] and 5.76 for thiourea with Au(I) [22]). Furthermore, they can exist under different forms, according to their **oxidation state**. So as to study the speciation of Pd, Pt and Au in this leach liquor, three analytical methods were employed: (i) UV spectrophotometry, that gives information about optical properties of complexes in solution, and indicates the presence or the absence of a peculiar complex (ii) CV and LHV to characterize the electrochemical activity of the metallic species, that is known to depend on its complex form and influenced by the nature of the ligand and (iii) CE which can evidence a mobility shift of the metallic species according to their global charge density and hydrodynamic radius, i.e. to their complexation and oxidation states.

Speciation of palladium in aqueous HCl solution: influence of thiourea

UV-Visible spectrophotometry

A diluted solution of Pd ($20 \mu\text{mol/L}$ in $\text{HCl } 0.1 \text{ mol/L}$), mimicking an artificial leach liquor, was studied by UV-visible absorption spectrophotometry in order to determine its optical properties and its complexation state (Fig.1 and Table 1). The spectrum of Pd (straight line) shows two absorption peaks at 222 nm ($24\,650 \text{ L.mol}^{-1}.\text{cm}^{-1}$) and 278 nm ($8370 \text{ L.mol}^{-1}.\text{cm}^{-1}$), with almost no variability after one-week storage at $+4^\circ\text{C}$ ($<10\%$). According to the literature [23], soluble Pd ion can exist in chloride media under two different **oxidation state** of $+II$ or $+IV$. It has been demonstrated by UV-Visible spectrophotometry that the chlorocomplexes remain in acidic media under a planar tetrachlorocomplex PdCl_4^{2-} ($+II$), and/or an octahedral complex PdCl_6^{2-} ($+IV$). The latter can be obtained in strong oxidative conditions [24], but is generally not observed in mild conditions. Our results are in good agreements with previous work [25], with a ratio $\epsilon_{222\text{nm}}/\epsilon_{278\text{nm}} = 2.95$ (versus 3.00 for $9.4 \mu\text{mol/L}$ Pd in 0.1 mol/L HCl in the literature), demonstrating that PdCl_4^{2-} remains the main complex in a solution at low pH and high chloride content, and is quite stable.

The addition of thiourea at different Pd:thiourea ratios ($1:1$ to $1:10$) induces an evolution in the optical properties of the solution, supported by visual observation. For ratios lower than $1:1$; a red-brown precipitate appears. Further addition of thiourea leads to an intense red coloration of the solution, that turns to a yellow clear coloration at ratio $1:4$ (tile curve), characterized by an absorption peak at $\lambda=246 \text{ nm}$ ($30\,255 \text{ L.mol}^{-1}.\text{cm}^{-1}$, Fig. 1). Higher ratio does not lead to any further visible modification of the solution, but shows a strong increase in the UV absorption at a wavelength of 236 nm . The addition of thiourea in the media has been previously studied [26]. Three different ratios

of Pd:thiourea in acidic solution have been described for **oxidation state** of +II : 1:1, 1:2 and 1:4. Our results are in good agreement with the literature, with a red-brown precipitate for ratio lower than 1:1 attributed to the formation of the dimer of $[\text{Pd}(\text{thiourea})\text{Cl}_2]_2$ [27]. The intense red color that appears between ratio 1:1 and 1:4 is attributed to $\text{Pd}(\text{thiourea})_2\text{Cl}_2$, slowly leading to the formation of $\text{Pd}(\text{thiourea})_4^{2+}$ for higher thiourea content. This latter complex has been studied and characterized, showing its stability in this medium [26, 28]. A speciation diagram is presented in Fig. S3 and is discussed below.

Capillary electrophoresis

The analysis of Pd artificial leach liquor (1 mmol/L Pd in HCl 0.1 mol/L) by CE (Fig. 2.a) presents a single peak at a negative electrophoretic mobility (I , $\mu_{\text{ep}} = -51.3 \pm 0.3 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) at both 222 and 270 nm wavelengths, with a ratio $\epsilon_{222\text{nm}} / \epsilon_{270\text{nm}} = 3.95$. Moreover, three minor peaks (2) are visible at a migration time lower than 2 min, one of them being attributed to NO_3^- , originating from the standard Pd solution. This result tends to prove the existence of Pd ion at +II, forming the PdCl_4^{2-} complex characterized by a ratio $\epsilon_{222\text{nm}} / \epsilon_{270\text{nm}}$ of 3.34 (obtained by a standard UV analysis by spectrophotometry). The difference in molar extinction coefficient ratio between CE and UV can be attributed to the fact that CE gives access to a separative dimension, contrary to spectrophotometry that analyzes the entire sample. Indeed, impurities such as nitrate ions have been identified here by CE at traces amount (Fig. 2.a). Another explanation concerning the difference in this ratio can arise from the possible equilibrium between PdCl_4^{2-} and PdCl_3^- .

Indeed, the sample is diluted in concentrated HCl (1 mol/L), whereas the BGE used for CE is composed of sodium chloride and lower amount of HCl (NaCl 50 mmol/L and HCl 1 mmol/L). Pd ion mobility is highly dependent on the chloride concentration of the BGE [29], the less is the chloride amount, the less is the electrophoretic mobility of the Pd complex, characteristic of the dissociation of PdCl_4^{2-} into PdCl_3^- . The optical properties of these two complexes are different [30], explaining why the ratio $\epsilon_{222\text{nm}} / \epsilon_{270\text{nm}}$ can be different from the one obtained by UV spectrophotometry.

Addition of thiourea in the sample leads to a drastic modification in peak electrophoretic mobility. The injection of a solution of Pd:thiourea ratio 1:4 in the BGE, void of thiourea, doesn't show any visible signal in negative polarity (-11kV). The inversion of polarity (+11 kV) leads to an asymmetric peak (Fig. 2.b, dashed line) at 246 nm, and a second very broad one. The addition of thiourea (2 mmol/L) in the BGE leads to a single peak in positive polarity at

246 nm (Fig. 2.b straight line, $\mu_{ep} = +34.1 \pm 0.2 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$), with a ratio $\epsilon_{246\text{nm}} / \epsilon_{270\text{nm}} = 1.36$. CE analysis corroborates the formation of $\text{Pd}(\text{thiourea})_4^{2+}$ at high thiourea concentration. Indeed, the hypothesis that the charge of the complex shifts from -2 to +2 should lead to an inversion of the migration direction of the complex under an electric field, especially under low electroosmotic mobility as it is the case in the considered BGE of low pH. When Pd sample is prepared in the BGE containing thiourea, and separated in a BGE void of thiourea, its complexed form $\text{Pd}(\text{thiourea})_4^{2+}$ seems to undergo a ligand exchange during separation (from thiourea to Cl) due to the large amount of chloride in the BGE, explaining the broad peak (Fig. 2.b, dashed line). The addition of thiourea in the BGE is then needed to stabilize the complex (Fig. 2.b, straight line), which can be identified by the ratio $\epsilon_{246\text{nm}} / \epsilon_{270\text{nm}} = 1.63$ (similar ratio obtained by a spectrophotometric analysis, Table 1). This result is of importance due to the fact that no electrokinetic characterization of this complex was reported in the literature to the best of our knowledge.

Cyclic voltammetry

CV were also conducted, as illustrated in Fig. 3. On the forward scan (from +1.2 V to -0.3 V), two reduction peaks are observed at -0.09 V (*I*, $E_{\text{red,I}}$) and -0.19 V (*II*, $E_{\text{red,II}}$). They are related to two distinct reduction processes. On the backward scan, the first re-oxidation process at -0.03 V (peak *III*) is related to reduction one (peak *II*), while the second re-oxidation one at 0.54 V (peak *IV*) corresponds to the cathodic reduction process *I* (Fig. 3.a). A previous study of PdCl_4^{2-} at different working electrodes [30–33] (carbon paste, palladium) reported the values of redox potential for the reduction of PdCl_4^{2-} to Pd metallic film at around -0.2 V vs. Ag/AgCl. Thus the first peak (*I*) can be attributed to the reduction of Pd(II) onto its metallic form according to **equation (1)**:

The second reduction peak (*II*) can be attributed to the adsorption of H^+ on the Pd film deposit [34]. The oxidation peak (*IV*) is typical of a stripping event, and can be attributed to the oxidation of the palladium film formed during the reductive scan (0.62 V/SCE in 1 mol/L HCl according to the literature [35]). LHV measurements (see Fig. 3.c) confirm the deposition that occurs at potential lower than 0 V, but also the stripping in oxidizing conditions. The Pd solutions were also analyzed by CV in presence of thiourea, as illustrated on Fig. 3.b. Conversely to Pd solution alone in HCl, no electrochemical reduction signal is observed in the potential range studied, for Pd:thiourea ratio 1:1 to 1:4, showing the occurrence of a chemical reaction. Moreover, for an excess of thiourea (Pd:thiourea ratio 1:10), an oxidation peak (*VI*) appears with $E_{\text{ox,e}} = +0.71 \text{ V/SCE}$. This oxidation process can be related to that of thiourea itself (in excess) since the potential value corresponds to that of the oxidation of thiourea alone in solution (*peak*

VII). As no electrochemical activity is visible for Pd:thiourea ratio prior to 1:4, it can be assumed that there is a complete chemical reaction between the metal ion and thiourea. The absence of reduction signal corroborates the change of Pd complex from PdCl_4^{2-} onto $\text{Pd}(\text{thiourea})_4^{2+}$, which is not reducible in the considered potential range (limited by the solvent reduction). Once the complex is formed, the excess of thiourea is then observed, as shown with the oxidation peak for high Pd:thiourea ratio. We could therefore state that Pd is at a +II. in this artificial leach liquor, either as a chlorocomplex (in HCl) or as a thio-chlorocomplex (in HCl and thiourea), allowing for the speciation diagram in Fig. S3.

Speciation of platinum in aqueous HCl solution: influence of thiourea

UV-Visible spectrophotometry

The UV visible spectra of Pt in artificial leach liquors are presented in Fig. 4 and data are summarized in Table 1. The solution of Pt in HCl exhibits a single absorption peak at 262 nm ($24\,930\text{ L.mol}^{-1}.\text{cm}^{-1}$). The storage of the solution at 4°C for 7 days shows no significant modification of the absorption spectrum, demonstrating the stability of the complex (< 10% of signal variation). The spectrophotometric characterization of Pt ion in HCl solution has been studied under different complex forms, such as hexachloroplatinic acid [36], showing that it exists under two different oxidation state of +II and +IV [23]. It is known that the complex PtCl_6^{2-} (+IV) is stable and can be detected by UV absorption at 202 nm ($\epsilon=49\,400\text{ L.mol}^{-1}.\text{cm}^{-1}$) and 262 nm ($\epsilon=24\,000\text{ L.mol}^{-1}.\text{cm}^{-1}$) [37], which is supposed to correspond to the Pt ion in solution (obtained in 0.1 mol/L HClO_4). Pt ion can also remain in solution at an oxidation state of +II, a planar tetrachlorocomplex of PtCl_4^{2-} , with an UV spectrum with a maximum absorption peak at around 220 nm [38]. Since no maximum intensity is measured at 220 nm, Pt ion exists only under its oxidation state of +IV in the artificial leach liquor, with a ratio $\epsilon_{202\text{nm}}/\epsilon_{262\text{nm}} = 3.67$ (versus 2.06 in the literature). The difference of ratio between the literature and our results is attributed to the presence of NO_3^- , which strongly absorbs at this wavelength. This ratio can thus not be used to clearly identify the chlorocomplex. .

The addition of thiourea induces changes in the optical properties supported by visual observation, depending on the Pt:thiourea ratio (1:1 to 1:10). These modifications are not as fast as for Pd: at least one day is required before complete stabilization. The results present the UV spectra 7 days after preparation. For Pt:thiourea ratio lower than 1:2, a red precipitate is formed. Further addition of thiourea induces the dissolution of the precipitate and yields to an intense yellow coloration of the solution, which turns to a yellow clear coloration for the ratio 1:4. This solution exhibits an absorption peak at 251 nm ($24\,915\text{ L.mol}^{-1}.\text{cm}^{-1}$), as shown on Fig. 4. Higher Pt:thiourea ratio do not lead

to any change of the solution, but a strong increase of the UV absorption at 236 nm is noticed, which corresponds to the absorption of thiourea. The effect of thiourea on Pt solution has been studied in the literature, notably for the synthesis of different complexes of Pt-thiourea [16]. It has been shown that Pt at oxidation state of +IV can be reduced by thiourea to an oxidation state of +II, giving a sub-product of formamide disulfide. Depending on the Pt:thiourea ratio, the resulting products were of different nature. For a ratio lower than 1:3, the main product was $\text{Pt}_2(\text{thiourea})_4\text{Cl}_6$ (with a mix of Pt oxidation states of +II and +IV), while for a ratio higher than 1:6, $\text{Pt}(\text{thiourea})_4\text{Cl}_2$ was produced (with only an oxidation state of +II). Our results tend to indicate a similar trend, with the shift in Pt ion oxidation state from +IV to +II, and the formation of the corresponding thiourea complex. For a ratio lower than 1:2, a red-brown precipitate appears, probably due to the formation of the dimer $[\text{Pt}_2(\text{thiourea})_4\text{Cl}_6]$ [16]. The yellow intense coloration for higher ratio is probably due to the formation of intermediate complexes till complete conversion into the $\text{Pt}(\text{thiourea})_4^{2+}$ complex. The UV signal at 236 nm for excess of thiourea corresponds to free thiourea in solution, as demonstrated by analysis of 40 $\mu\text{mol/L}$ thiourea in the same media (0.1 mol/L HCl) (Fig. 4).

Capillary electrophoresis

The CE separation of Pt 1 mmol/L in HCl 0.1 mol/L was performed in negative polarity, as shown on Fig. 5. The electropherogram exhibits three main peaks of negative electrophoretic mobility (1, $\mu_{\text{ep},1} = -68.0 \pm 0.6 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$; 2, $\mu_{\text{ep},2} = -77.6 \pm 0.6 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$; 3, $\mu_{\text{ep},3} = -38.4 \pm 0.1 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) with a ratio $\epsilon_{210\text{nm}} / \epsilon_{260\text{nm}} = 1.66$ for peak 1 (Fig. 5.a). It should be noted that the third peak (3) appears after storage of the solution for 7 days. Peak 1 can be attributed to PtCl_6^{2-} , characterized by a ratio $\epsilon_{210\text{nm}} / \epsilon_{260\text{nm}}$ of 2.04 obtained using a standard UV analysis by spectrophotometry. Peak 2 is attributed to NO_3^- , present in the standard Pt solution. Nevertheless, it is known in the literature [39] that PtCl_6^{2-} can be hydrolyzed under acidic condition into different forms. The third peak could be attributed to one of the sub-products, such as $[\text{PtCl}_5(\text{H}_2\text{O})]^-$.

Addition of thiourea in the sample up to a 1:4 ratio leads to the suppression of the characteristic peak of Pt in negative polarity. By inverting the separation polarity, one main peak (4) appears at 246 nm, in a BGE void of thiourea (Fig. 5.b). The addition of thiourea up to 2 mmol/L in the BGE leads to a better resolved and symmetric peak (5, $\mu_{\text{ep}} = +33.3 \pm 0.1 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). The CE experiments lead to the same conclusion as the one suggested for Pd *i.e* the formation of an instable complex of $\text{Pt}(\text{thiourea})_4^{2+}$ in the absence of thiourea in the BGE. The addition of thiourea in the BGE (Fig 5.b) leads to the stabilization of the Pt/thiourea complex. This result is of importance due to the fact that no electrokinetic characterization of Pt/thiourea complex was reported in the literature to our knowledge.

Cyclic voltammetry

CV was also performed with the Pt solution in absence of thiourea (Fig. 6.a). An ill-defined reduction signal (*I*) is observed on the forward scan starting at around -0.05 V (Fig. 6.a), limited by reduction of the solvent, while a re-oxidation peak (*II*) is observed at +0.93 V. In the presence of thiourea (Fig. 6.b), no reduction signal is observed for a 1:10 ratio, but two oxidation peaks (*III*, $E_{\text{ox,III}} \approx +0.71$ V ; *IV*, $E_{\text{ox,IV}} = +0.89$ V) are visible. The exact mechanism for PtCl_6^{2-} reduction has been discussed in the literature and is questionable. Some studies made the assumption of Pt deposition during reduction through multiple reactions pathway [32], but no observation was made in agreement with an electrodeposition process in the absence of thiourea. The importance of hydrolysis state of the complex (mono- or bi-hydrated) has been highlighted, but according to our measurements, the complex may be reduced at the electrode into an **oxidation state** of +II, with no visible deposition at the electrode on the LHV experiment (Fig. 6.c). $\text{Pt}(\text{thiourea})_4^{2+}$ can be oxidized into a new complex of **oxidation state** of +IV since an oxidation peak (*IV*) has been shown on CV measurement (Fig. 6.b). Peak *IV* can be attributed to thiourea since the ligand itself shows an oxidation peak corresponding to the same potential value. LHV of ratio 1:10 (see Fig. 6.c) presents no reduction wave, while two oxidation waves are observed, the first being attributed to free thiourea and the second to Pt complex of thiourea. As a conclusion, it can be assumed that Pt ion in artificial leach liquor is at an **oxidation state** of +IV, as a $\text{Pt}(\text{Cl})_6^{2-}$ complex, quite stable in the media, reducible by thiourea, and forming $\text{Pt}(\text{thiourea})_4^{2+}$ in excess of the organic ligand.

Speciation of gold in aqueous HCl solution: influence of thiourea

UV-Visible spectrophotometry

The characterization of soluble Au in HCl 0.14 mol/L was performed the same way as for the other metals. UV absorption spectra are shown in Fig. S4 and data are summarized in Table 1. The solution of gold in HCl exhibits two absorption peaks at 226 nm ($43\,780\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and 311 nm ($7\,250\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). These two peaks are attributed to AuCl_4^- complex, with Au at an **oxidation state** of +III [40]. The wavelengths values are dependent on the pH of the solution, due to ligand exchange between chloride and hydroxide ion. In our experimental conditions, the pH is sufficiently low (pH=1) to stabilize the gold tetrachlorocomplex, as suggested by its stability after 7 days storage at 4°C (<10%). The addition of thiourea at different Au:thiourea ratio (1:1 to 1:10) leads to changes of the optical properties supported by visual observation. Changes are slower than for Pd ion but faster than for Pt ion, with an evolution over one day. For a ratio below 1:1, an orange precipitate appears in solution. Further addition of thiourea leads to an intense yellow coloration and complete disappearance of the precipitate, which turns to a yellow

clear coloration for the ratio 1:4, with an absorption peak for a wavelength of 242 nm ($\epsilon=17\,610\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). Similarly to Pd and Pt ion, higher ratio doesn't lead to any visible change of the solution, but shows a strong increase of the UV absorption for a wavelength of 236 nm (Fig. S4). It was reported that Au at oxidation state of +III can be reduced by thiourea to an oxidation state of +I [13]. The difference with Pt ion is that the Au ion will react differently as a function of the concentration of thiourea. Actually, Au^+ in absence of thiourea in HCl will form the chlorocomplex of AuCl_2^- , that disproportionates as described below (Equation 2) in low thiourea content. The precipitate observed at low Au:thiourea ratio solution is attributed to the formation of metallic gold particles that seem to aggregate under these conditions according to this reaction. But for higher thiourea content (ratio 1:4 and more), the Au ion at oxidation state +I can form a new complex of $\text{Au}(\text{thiourea})_2^+$, quite stable in the media [41] according to our results (with no evolution of the UV spectra after 7 days). Free thiourea remained in solution after the reaction, proved by the absorption peak at 236 nm, characteristic of the absorption of thiourea ligand.

Capillary electrophoresis

The analysis of the gold solution in absence of thiourea is shown in Fig. 7.a. A main peak is observed and detected at 222 nm ($1, \mu_{\text{ep},1} = -47.0 \pm 0.2 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). This single peak can be attributed to AuCl_4^- complex in solution since blank samples gave no peak. The other peaks are attributed to the matrix composition.

Thiourea addition in the sample leads to the suppression of the CE peak characteristic of AuCl_4^- . CE experiments corroborate the transformation of AuCl_4^- into $\text{Au}(\text{thiourea})_2^+$ (for high thiourea content). The inversion of the separation polarity (Fig. 7.b) gives one peak (3), like those obtained with Pd or Pt ion. $\text{Au}(\text{thiourea})_2^+$ seems to be destabilized in a BGE without thiourea, as for Pd and Pt ion. It is possible to obtain a stabilized peak (4, $\mu_{\text{ep},4} = +23.3 \pm 0.1 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) by adding thiourea in the BGE, in order to stabilize the Au/thiourea complex. This result is of importance due to the fact that no electro-kinetic characterization of this complex has been performed to our knowledge.

Cyclic voltammetry

The analysis of gold solution by CV in absence of thiourea shows a reduction peak I at +0.35 V (Fig. 8.a), while an oxidation one (II) appears on the forward reverse scan at +1.00 V. AuCl_4^{2-} is reduced and deposited to form Au metallic layer through the reduction (a) of AuCl_4^- complex into AuCl_2^- . Actually, Au(I) has been described in the literature [40, 42–46] as unstable under certain conditions.

This complex can dismutate according to equation (2):

This reaction leads to the formation of a metallic film, which is then oxidized (*II*) at higher potential, giving the typical stripping peak, similar to the behavior of Pd ion. LHV measurements (see Fig. S5) confirm the deposition that occurs at potential lower than +0.35V, but also the stripping in the oxidizing condition. Depending on thiourea amount in solution, CV measurements (Fig. 8.b) show significant differences. For ratio 1:4, there are three-oxidation peaks (*III*, $E_{ox,III} = +0.43$ V ; *IV*, $E_{ox,IV} \approx +0.77$ V ; *V*, $E_{ox,V} \approx +1.00$ V) and one reduction feature for low potential values (*VI*, $E_{red,VI} < -0.2$ V). In presence of larger thiourea content, the voltammogram shows one reduction peak (not as intense as for lower ratio) and one oxidation process (*VII*, $E_{ox,VII} = +0.71$ V). For Au:thiourea ratio of 1:4, the amount of thiourea is not sufficient to convert all $AuCl_4^-$ into the thiourea complex. Since a complete reaction between thiourea and Au ion after 7 days storage seems to occur, one can suppose that no free thiourea remains in solution (no signal corresponding to thiourea is observed on CV experiment). The reduction signal *VI* (Fig.8.b) can be associated to the reduction of the newly formed $Au(thiourea)_2^+$ complex into Au layer, while the oxidation peak *V* could correspond to the oxidation of the metallic film formed during the reduction step. Signal *VII* could be attributed to the oxidation of residual thiourea onto the modified electrode. In excess of thiourea, it can be concluded that $AuCl_4^-$ complex is converted into $Au(thiourea)_2^+$, which can be reduced into Au metallic deposit, while free thiourea remain in solution (attributed to peak *VII*). The stripping of Au^0 through its oxidation is overlapped by thiourea signal. The reduction of $AuCl_4^-$ by thiourea in solution can be demonstrated by immersing the working electrode in a solution containing the Au complex and thiourea (Fig. 8.c). The CV obtained after transfer of this electrode to a fresh HCl solution (without Au and thiourea) show a more and more intense oxidation signal while the electrode was immersed a longer time prior to the analysis. This oxidation signal is attributed to the dissolution of Au film that spontaneously formed at the electrode while thiourea reacts with $AuCl_4^-$ to give Au at an oxidation state of +I, that adsorbs at the electrode and further disproportionate to give Au^0 (2). The low amount of thiourea leads then to the disproportionation of $AuCl_2^-$ into the metallic film.

Also, by varying the scan rate during CV experiment on $AuCl_4^-$ (see Fig. S6), the electro-reduction of $AuCl_4^-$ was proven as being a diffusion controlled process [47]. Furthermore, no reduction signal was observed by CV after transfer of the electrode in HCl. Thus, it can be deduced that no $AuCl_4^-$ is adsorbed onto the surface. The gold

deposition occurs on the carbon electrode when adding thiourea in the solution upon adsorption of AuCl_2^- species generated by reduction of the initial tetrachlorocomplex by thiourea.

Real sample quantitation

Finally, real PCBs leach liquors (named LL) and 1 mol/L HCl solutions as controls named (HCl) were prepared and analyzed, either pure or spiked with Pd and Au (10 mg/L, named LLsp, HClsp, respectively) as described in section 2.5. Solutions LL_A (filtered sample), LL_B (sample matrix from loading step) and LL_C (elution fractions, i.e. LL_{C1} , LL_{C2} and LL_{C3}) of each leach liquor or HCl control, either pure or spiked, have been characterized using UV spectrophotometry, voltammetry and CE so as to identify and quantify the presence of precious metals and evaluate extraction process efficiency. Relevant characterizations obtained with each method are summarized in Table 2.

3.4.1 UV-Visible spectrophotometry

LL_A exhibits a UV absorption signal for wavelength values inferior to 300 nm, with a maximum at about 235 nm which is a characteristic wavelength of both chlorocomplexes of palladium and gold (Table 1). This can be attributed to solubilized PCB compounds, resulting from the leaching process with 0.18 % (w/v) H_2O_2 in 1 mol/L HCl, as no signal was obtained for HCl used as blank. In this manner, it can be assumed that the weak amount of H_2O_2 initially present in the oxidative medium was totally consumed during the leaching process. The UV spectrum of LL_B displays the same characteristic pattern as LL_A but with overall reduced intensities that tend to indicate the retention of the absorbing compounds of interest on the extraction column. The solution collected as waste during the washing step gave no specific UV signal, just as pure 1 mol/L HCl rinsing solution, indicating no detectable desorption of absorbing compounds in acidic medium.

Regarding LLsp and HClsp (10 mg/L Pd and Au final concentration), the corresponding filtered solutions display the same characteristic UV absorption pattern with a main peak at 263 nm and a weak shoulder at 235 nm. Respective solutions collected as waste during the loading and washing steps both showed the disappearance of the weak shoulder at 235 nm and the persistence of the maximum at 263 nm. This is consistent with previous conclusions that tend to prove the selective retention of absorbing compounds that

could be chlorocomplexes of Au and Pd while an impurity detected at 263 nm in the spiked samples is eluted through the loading and rinsing steps[20].

Since the eluated fractions LL_C and HCl_C contain high concentration of thiourea (0.5 mol/L), a strong UV signal was measured at wavelength below 300 nm, leading to detector saturation. Thus, no characteristic UV absorption pattern could be obtained.

3.4.2 Cyclic voltammetry

Concerning the electrochemical properties of solutions LL_A and LL_B , both show an oxidation peak at 0.785 ± 0.010 V/SCE associated to a reduction process at 0.09 ± 0.01 V/SCE. These signals are attributed to the presence in solution of electroactive compounds resulting from the leaching process and that are not retained by the extractant. As a control, HCl_A and HCl_B solutions show no signal in the same potential range. After spiking, LL_{sp_A} gave a supplementary oxidation peak at + 0.63 V/SCE, which can be attributed to Pd (II), Au oxidation peak being potentially overlapped with the matrix peak (+0.79 V/SCE). Solution LL_{sp_B} shows only one oxidation peak at 0.795 V/SCE, due to the matrix compound, and indicating the selective retention of Pd on the adsorbant. This is consistent with the voltammograms solutions since similar oxidation signals (+0.66 and + 0.89 V/SCE for Pd and Au oxidation respectively) in the solution .

All the eluated solutions contain high concentration of thiourea, thus interfering oxidation signals originating from the ligand did mask the electrochemical response of any other electroactive compound in the range 0.2 to 1.2 V/SCE. Therefore, no characteristic electrochemical pattern could be obtained.

3.4.2 : Electrokinetic quantitation

In order to demonstrate the extraction yield efficiency of the all procedure, solutions LL_C were analyzed by CE so as to evidence the potential presence of thiourea-complexes of precious metals. The extraction yield was estimated on the basis of a theoretical expected concentration of thiourea complexes equal to 66.7 mg/L in Pd and Au, based on 100 % recovery and a 6.67 concentration factor (volume ratio in between solution A and solution C-1).

Solution LLsp_{C1} (Fig.9.a) gave 3 resolved peaks (1, $\mu_{ep,1} = -44.1 \pm 1.5 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$; 2, $\mu_{ep,2} = -36.1 \pm 1.4 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$; 3, $\mu_{ep,3} = -27.9 \pm 1.3 \cdot 10^{-5} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$). Since no significant peak could be identified when analyzing solutions LLsp_{C2} and LLsp_{C3} (due to the absence of metals in solution or in quantity inferior to the LOD), attention was given to the results obtain on solution LLsp_{C1}. Peak 1 was attributed to Pd(thiourea)₄²⁺ and peak 2 to Au(thiourea)₂⁺ by individual separation of each metal complex, prepared in 0.5 mol/L thiourea / 0.1 mol/L HCl. CE-UV allowed the quantitation of thiourea complexes, after determination of the calibration curves for each complex in a concentration range from 25 to 125 mg/L (Fig.9.b), leading to limits of detection of 1.2 and 3.8 mg/L for thiourea complexes of Pd and Au, respectively, which is inferior to what is expected for real solutions (with final concentration of thiourea complexes superior to 5 mg/L). The extraction yield of Pd- and Au-thiourea complexes obtained from solution LLsp_{C1} are reported in Fig.9.c for both HClsp (taken as blank) and LLsp. Extraction yields of 94 % and 101±13 % (n=3, on independent cartridges) for Pd and 85% and 37±10 % for Au were calculated for HClsp and LLsp, respectively. Thus solutions at a final concentration of 67.6±8.5 mg/L in Pd and 27.6±6.4 mg/L in Au were obtained after purification and extraction of the spiked leach liquor on the cartridge.

A matrix effect can be highlighted here on the extraction yield of Au, decreasing from 85% in HCl to 37 % in leach liquor. This can be due to Au complexation by matrix agents, thus changing the interaction nature between the extractant and the metal or by competition between Au-chlorocomplexes and an interferent potentially retained by the cartridge, as suggested by the detection of a third peak in solution LLsp_C of spiked and non-spiked leach liquor (results not shown). This peak could be tentatively assigned to the presence of copper in leach liquor matrix since the analysis of a 5 mmol/L CuCl₂ solution prepared in 0.5 mol/L thiourea / 0.1 mol/L HCl gave a peak of similar assymetry and migration time in capillary zone electrophoresis. Furthermore, the CE analysis of solution LLsp_{C1} resulting from leach liquor spiked with only Au gave a recovery efficiency of 111%, meaning that the loss of efficiency could probably originate from a competing effect with Pd. Complementary purification steps could be proposed to increase the recovery of Au, varying the cartridge composition or thiourea concentration. Therefore CE appears as a very interesting methodology to precisely determine the concentration in leach liquors, and to help for controlling extraction processes for strategic metal recycling.

Conclusion

The speciation of Pd, Pt and Au was studied by different methodologies (UV-Visible spectrophotometry, cyclic voltammetry and capillary electrophoresis) in leach liquors that mimic leaching treatments (HCl liquors with or without thiourea) before recycling processes. UV spectra allowed identifying chlorocomplexes in HCl solution and evidencing the presence of different thiourea complexes when adding thiourea at different concentrations in HCl solutions. A difference in the kinetics of thiourea complexation in this leach liquor was demonstrated for three precious metals. It was shown that thiourea reduces Pt and Au, leading to new complexes depending whether on the concentration of thiourea and chloride ion in the media, while ligand exchange happens for Pd ion with no **oxidation state** change. CE separation in the different BGEs confirmed the formation and stability of these identified complexes, according to BGE composition. Furthermore, the electrochemical activities of chloro- and thiourea- complexes were determined by CV, indicating that thiourea complexes did not present any apparent electrochemical activity in the potential range of study. Thanks to these three methodologies, the speciation of Pd, Pt and Au could be established in these specific conditions mimicking the leaching process, opening the way for a deeper understanding and control of the different steps for developing new recycling processes of these strategic metals from WEEE.

Besides, CE proved to be a powerful methodology for rapid and easy quantitation of leach liquors, before processing to precious metal recovery and valorization. With a LOD of 1.2 and 3.8 mg/L for Pd and Au-thiourea complexes respectively, inferior to the metals concentration in leach liquors, CE was used to estimate the extraction yield of a solid phase extraction process by quantitation of thiourea complexes in spiked leach liquor. The extraction yields for each metal separately was determined as 100%, and possible matrix interference or metal competition was evidenced. Therefore CE was proved as a very interesting methodology to precisely quantitate strategic metals in leach liquors, opening the way for an automated control of extraction processes for strategic metal recycling.

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Figures Captions

Fig. 1 UV absorption spectra of Pd solution with or without thiourea at different molar ratios. Straight line: fresh 20 $\mu\text{mol/L}$ Pd in 0.1 mol/L HCl. Dash line: 20 $\mu\text{mol/L}$ Pd in 0.1 mol/L HCl after 7 days storage. Dotted line: 40 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl. Square: 20 $\mu\text{mol/L}$ Pd + 20 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl. Tile: 20 $\mu\text{mol/L}$ Pd + 80 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl. Triangle: 20 $\mu\text{mol/L}$ Pd + 200 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl

Fig. 2 Electrophoretic separation of Pd ion (a) 1 mmol/L diluted in 0.1 mol/L HCl, separated in BGE (50 mmol/L NaCl / 1 mmol/L HCl) under a voltage of -11 kV and detected at 222 and 270 nm. (b) 1 mmol/L diluted in 10 mmol/L thiourea / 0.1 mol/L HCl, separated in BGE with or without 2 mmol/L thiourea under a voltage of +11 kV, and detected at 246 nm. Separation conditions: Fused silica, capillary length 35 cm; detector 26.5 cm; 50 μm internal diameters. Injection condition: successive injections of sample and BGE (30 mbar during 2 s)

Fig. 3 (a) Cyclic voltammetry at glassy carbon electrode of palladium solutions in HCl (scan rate 100 mV/s). Straight line: fresh Pd 1 mmol/L in HCl 0.1 mol/L after preparation. Dash line: Pd 1 mmol/L in HCl 0.1 mol/L after 7 days storage. Dotted line: HCl 0.1 mol/L. (b) Cyclic voltammetry at glassy carbon electrode of palladium solutions in HCl and thiourea (scan rate 100 mV/s). Straight line: Pd 1mmol/L + thiourea 4 mmol/L in HCl 0.1 mol/L. Dashed line: Pd 1mmol/L + thiourea 10 mmol/L in HCl 0.1mol/L. Dotted line: thiourea 2 mmol/L in HCl 0.1 mol/L. (c) Linear hydrodynamic voltammetry of a solution of Pd 1 mmol/L in HCl 0.1 mol/L at glassy carbon electrode at 0.1V/s. Straight line: Pd 1 mol/LM in HCl 0.1 mol/L after preparation, from -0.3 to +1.2 V. Dash line: Pd 1 mmol/L in HCl 0.1 mol/L after preparation, from +0.9 to -0.3 V

Fig. 4 UV absorption spectra of platinum solution with or without thiourea at different molar ratios. Straight line: fresh 20 $\mu\text{mol/L}$ Pt in 0.1 mol/L HCl. Dash line: 20 $\mu\text{mol/L}$ Pt in 0.1mol/L HCl after 7 days storage. Dotted line: 40 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl. Square: 20 $\mu\text{mol/L}$ Pt + 20 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl. Tile: 20 $\mu\text{mol/L}$ Pt + 80 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl. Triangle: 20 $\mu\text{mol/L}$ Pt + 200 $\mu\text{mol/L}$ thiourea in 0.1 mol/L HCl

Fig. 5 Electrophoretic analysis of Pt ion (a) 1 mmol/L diluted in HCl 0.1 mol/L, separated in BGE (NaCl 50 mmol/L / HCl 1 mmol/L) under a voltage of -11 kV, and detected at 210 and 260 nm. (b) 1 mmol/L diluted in thiourea 10 mmol/L / HCl 0.1 mol/L, separated in BGE with or without 2 mmol/L thiourea under a voltage of +11kV, and detected at 246nm. Separation conditions: Fused silica, capillary length 35 cm ; detector 26.5 cm ; 50 μm internal diameters. Injection condition: successive injections of sample and BGE (30 mbar during 2 s)

Fig. 6 (a) Cyclic voltammetry at glassy carbon electrode of Pt in HCl (scan rate 100 mV/s). Straight line: fresh Pt 1 mmol/L in HCl 0.1mol/L after preparation. Dash line: Pt 1 mmol/L in HCl 0.1 mol/L after 7 days storage. Dotted line: HCl 0.1 mol/L. (b) Cyclic voltammetry at glassy carbon electrode of Pt in HCl and thiourea (scan rate 100 mV/s). Straight line: Pt 1 mmol/L + thiourea 4 mmol/L in HCl 0.1 mol/L. Dash line: Pt 1 mmol/L + thiourea 10 mmol/L in HCl 0.1 mol/L. Dotted line: thiourea 2 mmol/L in HCl 0.1 mol/L. (c) Linear hydrodynamic voltammetry of different platinum solutions at glassy carbon electrode at 0.1V/s. Straight line: Pt 1 mmol/L in HCl 0.1 mol/L after preparation, from -0.3 to +1.2 V. Dash line: Pt 1 mmol/L in HCl 0.1 mol/L after preparation, from +1.2 to -0.3 V. Thin dash line: Pt 1 mmol/L + thiourea 5 mmol/L in HCl 0.1 mol/L 7 days after preparation, , from -0.3 to +1.2 V

Fig. 7 Electrophoretic separation of Au ion (a) 0.5 mmol/L diluted in HCl 0.14 mol/L, separated in BGE (NaCl 50 mmol/L / HCl 1 mmol/L) under a voltage of -11 kV, and detected at 222 and 270 nm. (b) 0.5 mmol/L diluted in thiourea 5 mmol/L / HCl 0.14 mol/L, separated in BGE with or without 2 mmol/L thiourea under a voltage of +11 kV, and detected at 246 nm. Separation conditions: Fused silica, capillary length 35 cm; detector 26.5 cm; 50 μm internal diameters. Injection condition: successive injections of sample and BGE (30 mbar during 2s)

Fig. 8 (a) Cyclic voltammetry at glassy carbon electrode of Au solutions in HCl (scan rate 100 mV/s). Straight line: fresh Au 0.5 mmol/L in HCl 0.14 mol/L. Dash line: Au 0.5 mmol/L in HCl 0.14 mol/L after 7 days storage. Dotted line: HCl 0.14 mol/L; (b) Cyclic voltammetry at glassy carbon electrode of Au solutions in HCl and thiourea (scan rate 100 mV/s). Straight line: Au 0.5 mmol/L + thiourea 2 mmol/L in HCl 0.14 mol/L. Dash line: Au 0.5 mmol/L + thiourea 5 mmol/L in

HCl 0.14 mol/L. Dotted line: thiourea 2 mmol/L in HCl 0.1 mol/L. CV from +1.2 to -0.3 to +1.2, 100 mV/s ; (c) Straight line: Right after immersion of the WE in freshly prepared 0.5mmol/L Au, 0.5 mmol/L thiourea in 0.1 mol/L HCl. Dash line: 1 min after immersion of the WE in the same media. Dotted line: 10 min after immersion of the WE in the same media

Fig. 9 (a) CE analysis of Solutions C1 to C3 collected as 3 successive fractions of 3.75 mL after the treatment on Analig® PM-07 SPE cartridge of a Pd- and Au-spiked leach liquor; (b) calibration curve for the quantitation of Pd and Au -thiourea complexes (at 246 nm) by CE-UV (metals prepared in 10 mmol/L Thiourea / 0.1 mol/L HCl; it can be noticed that error bars were calculated and smaller than the used marker size), and (c) calculated extraction yield for Pd- and Au-spiked samples (leach liquor and 1 mol.L⁻¹ HCl solution).

Table 1 Reported values of Absorption Coefficient ϵ ^[a] corresponding to maximum absorption peaks of UV spectra of Pd, Pt and Au ion in solution

Identified Species	λ_1 (nm)	ϵ_1 (L/(mol.cm))	λ_2 (nm)	ϵ_2 (L/(mol.cm))	ϵ_1/ϵ_2	Observed color	Ref.
PdCl ₄ ²⁻	223	24339	279	8113.4	3.00	-	[25]
	222	24650 ± 499	278	8370 ± 167	2.95	Yellow clear	This work
Pd(thiourea) ₄ ²⁺	-	-	-	-	-	Light Yellow (in HCl/HNO ₃)	[14]
	246	30255 ± 605	300	13875 ± 278	2.04	Yellow clear	This work
thiourea	236	12023	-	-	-	Colorless	[48]
	236	13150 ± 263	-	-	-	Colorless	This work
PtCl ₆ ²⁻	202	49400	262	24000	2.06	-	[37]
	202	91465 ± 1829 ^[b]	262	24930 ± 499	3.67	Yellow clear	This work
PtCl ₄ ²⁻ (data not shown)	217	12102	-	-	-	-	[38]
	216	12560 ± 251	-	-	-	Yellow clear	This work
Pt(thiourea) ₄ ²⁺	-	-	-	-	-	Yellow green (in HCl/HNO ₃)	[14]
	251 ^[c]	24915 ± 498	-	-	-	Yellow clear	This work
AuCl ₄ ⁻	226	-	311	-	-	Yellow clear	[40, 49]
	226	43780 ± 876	311	7250 ± 145	6.04	Yellow clear	This work
Au(thiourea) ₂ ⁺	-	-	-	-	-	-	-
	242	17610 ± 352	-	-	-	Yellow clear	This work

[a] ϵ was calculated according to Beer-Lambert Law. [b] Presence of nitrate in the artificial leach liquor leads to a strong absorption of the signal below 220 nm. [c] Peak undefined after 7 days storage. Defined for Pt:thiourea 1:4.

Table 2 - Characterization of untreated leach liquor, as well as leach liquor matrix and analyte recovery fractions after processing on Analig® PM-07 cartridge

Sample nature	A (filtered sample)	B (sample matrix from loading step)	C 1 (first elution fraction)
HCl (1 M HCl)	CV	-	X
	UV	-	X
	CE	-	-
HClsp (Spiked HCl)	CV	+660 mV / +890 mV	X
	UV	263 nm	X
	CE	-	[Pd] = 60.9 mg/L
	CE	-	[Au] = 52.8 mg/L
LL (Leach liquor)	CV	+785 ± 10 mV	X
	UV	235 nm	X
	CE	-	Cu presence
	CE	-	Cu presence
LLsp (Spiked LL)	CV	+630 mV / +790 mV	X
	UV	263 nm	X
	CE	-	[Pd] = 66.2 mg/L
	CE	-	[Au] = 20.6 mg/L
			Cu presence

(-) no signal; (X) saturation of the detector / signal