Extraction, separation and recovery of palladium and platinum by a kinetic method combined with ultrafiltration

Tarita Biver, Clara Paoletti, Fernando Secco *, Marcella Venturini

Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy

HIGHLIGHTS

- Pd(II) reacts with the extracting ligand PADA much faster than Pt(II).
- Pd(II)/PADA neutral complex is adsorbed on SDS micelles and extracted (ultrafiltration).
- Pt(II) is not adsorbed and is separated from Pd(II) (98% yield).
- Pd(II) can then be recovered from the micelles using stripping agents (90% yield).

GRAPHICAL ABSTRACT

Separation of palladium (II) from platinum(II) is achieved by a simple method, based on the different kinetic lability of the two metals, that could be of general application.
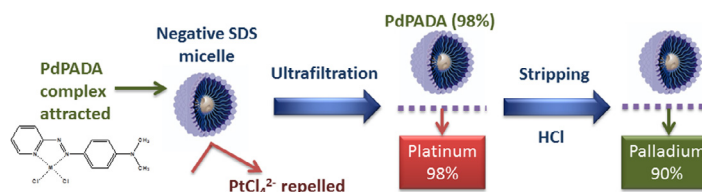
ARTICLE INFO

ABSTRACT

A method is presented allowing separation of palladium from platinum based on the different kinetic lability of the two metals. These are let to react with PADA (*trans*-pyridine-2-azo-*p*-dimethylaniline) in the presence of SDS micelles. The kinetic study of the PADA binding to Pd(II) and Pt(II), both in form of chlorocomplexes, shows that the reactivity of $PdCl_4^{2-}$ is about 4×10^3-fold higher than that of $PtCl_4^{2-}$. The Pd(II)–PADA complex is completely formed in about 30 min and adsorbed on the micelle surface. In this lapse of time less than 2% of Pt(II) is complexed. The separation of the two metals is then accomplished by ultrafiltration. With this procedure 98% of platinum can be recovered in the filtrate. Palladium, present in the retentate, is then recovered using a stripping agent and a multi-step ultrafiltration procedure. The most efficient among the stripping reagents tested is HCl 0.05 M (yield 90% after three steps). The extraction yield is independent of the concentration of the SDS micelles ([SDS] = 0.01–0.04 M), thus allowing low concentrations of surfactant to be used with excellent yields.

1. Introduction

Palladium and platinum are precious metals that have enormous importance not only in jewelry but also for their increasing use in the modern industry. These metals play a fundamental role in nowadays chemical technologies [1–4]. Because of the dangerous release in the environment of platinum and palladium [5,6] and of the continuous increase of the industrial demand of these rare metals, it becomes interesting to invent and develop new chemical processes for their extraction, separation and recovery, even from matrices containing low concentrations of these species.

From the analytical chemistry point of view, reliable and robust methods to quantify the content of such metals in the target sample need to be developed. The possibilities and areas of application of chemical test methods are constantly expanding. Among these, sorption-spectroscopic methods based on photometry and diffuse reflection spectroscopy and reagent indicator papers can be cited [7]. Other optical methods can also be envisaged. For instance, a sensitive fluorescent indicator for Pt(IV) and Pd(II) ions was found to allow the determination of trace concentrations of these metals both in active pharmaceutical ingredients and geological samples

* Corresponding author. Tel.: +39 0502219259; fax: +39 0502219260.
E-mail addresses: tarita@dcci.unipi.it (T. Biver), clara.paoletti@libero.it (C. Paoletti), ferdi@dcci.unipi.it (F. Secco), marcella@dcci.unipi.it (M. Venturini).

and in soils [8]. The spectroscopic mass techniques as ICP-MS play a major role [9] but it was also observed that non-negligible interferences between platinum group metals can occur [10]. To alleviate these problems, cationic and anionic exchangers and tellurium precipitation have been used most frequently prior to determination by ICP-MS [11] but these methods are cumbersome and time consuming. Separation and pre-concentration of platinum was accomplished making use of an acid induced mixed-micelle mediated cloud point extraction [12,13]. The unique properties of surfactants make them flexible agents for different miniaturized sample preparation techniques and the use of surfactants with different roles in sample-preparation methodologies is an important contribution to minimizing the problems arising from preliminary operations, which are the weakest step in analytical measurement [14].

The micellar approach coupled with ultrafiltration (micellar enhanced ultrafiltration – MEUF) can indeed be considered as a good tool to remove heavy metals from water solutions using micelles [15–18].

Micellar systems can be used in the studies on metal ions complexation as they are able to drive the complexation process into the desired direction [19,20]. In our group we have a consistent background in the analysis of metal ions reactivity in the presence of micellar phases [21–25] and of the kinetic analysis of palladium containing systems [26,27]. On this basis, it was considered that it could be of some interest to investigate if the MEUF approach could be used as a simple tool to achieve platinum and palladium separation and recovery.

In this paper we describe a method for extraction and separation of Pd(II) and Pt(II), originally present in mixtures, which makes use of *trans*-pyridine-2-azo-*p*-dimethylaniline (PADA) as the complexing ligand and of SDS micelles as the medium absorbing the metal–PADA complex. PADA was chosen because of its excellent interaction with the SDS surface (100% absorption) and high reaction rate with respect to other similar complexing agents [28]. In order to find the optimal conditions for the separation procedure, a kinetic study of the binding of PADA to $PdCl_4^{2-}$ and $PtCl_4^{2-}$ has been performed.

2. Experimental

2.1. Materials

K_2PdCl_4 (purity 99.99%), K_2PtCl_4 (purity 99.99%), PADA (*trans*-pyridine-2-azo-*p*-dimethylaniline, purity 98%) and SDS (sodium dodecylsulphate, purity > 99%, critical micellar concentration (CMC) = 8×10^{-3} M [25]) were purchased from Sigma–Aldrich Co. Stock solutions were prepared by dissolving the salt in acidic aqueous solution. Sodium chloride and perchlorate were obtained from Fluka, while magnesium chloride and sodium chloroacetate were from Carlo Erba. The buffer solutions used for electrode calibration were from Merck. All reactants were analytical grade and were used without further purification. All solutions were prepared by using doubly deionized water.

An ultrafiltration membrane made of regenerated cellulose (YM 3, Millipore) of diameter 44.5 mm and with a molecular weight cut off (MWCO) of 3000 Da was used in the ultrafiltration experiments.

2.2. Methods

Measurements of pH were made using a combined glass electrode (Metrohm 6.0234.100) in connection with a Metrohm 713 pH meter. The electrode calibration was made using buffer solutions between pH 4.00 and 9.00 ($\pm$0.02 pH units). Small amounts of

chloroacetate/chloroacetic acid buffer were added to the working solutions to keep the pH constant.

The amounts of metal ions in the initial solutions and in the permeates were assessed by atomic absorption spectroscopy using a Perkin Elmer AAnalyst 100 apparatus. Samples were atomized in a graphite furnace. The amounts of metal ions in the retentate were determined from mass balance.

Complex formation kinetics and equilibria were investigated using a Perkin-Elmer Lambda 35 spectrophotometer. Kinetic studies concerning the Pd(II)/PADA complex formation were monitored at $\lambda = 636$ nm (maximum absorption of the Pd(II)/PADA complex), at constant [PADA] = $C_L = 5 \times 10^{-6}$ M and changing metal concentration in the range $C_M = 3.5 \times 10^{-5}$–3.0×10^{-4} M (pH 3.9, $T = 25$ °C). Pt(II)/PADA complex formation was monitored at $\lambda = 556$ nm (maximum absorption of free PADA), at constant [PADA] = $C_L = 5 \times 10^{-6}$ M and changing metal concentration in the range $C_M = 5.0 \times 10^{-5}$–5.1×10^{-4} M (pH 3.9, $T = 25$ °C). Calibrated amounts of the metal containing solutions were added to 2 mL of PADA solution already contained in the spectrophotometric cell which was thermostatted at 25 °C. The mixing of the reactants was completed in a time lapse (5 s) much shorter compared to the course of the reaction. In the case of Pd(II), the absorbance versus time curves were automatically recorded by the instrument and saved on a computer. In the case of Pt(II), the reaction is too slow for its temporal course to be recorded automatically, so a batch-wise procedure was adopted which consisted in the absorbance measurements of samples of the reacting mixtures at given time intervals. The kinetic curves were analyzed by non-linear least-square procedures using the program Jandell.

Spectrophotometric titration for the system Pd(II)/PADA was carried out by adding increasing volumes of $PdCl_4^{2-}$ solution to the cell containing 2.0 ml of PADA solution. The temperature of the experiments was 25 °C.

Ultrafiltration experiments were carried out in batch stirred cells (Amicon, model 8050) with a capacity of 50 ml and an effective membrane area of 13.4 cm^2. In the metal extraction and separation procedure, suitable amounts of PADA and SDS were added to the solution containing $PdCl_4^{2-}$ and $PtCl_4^{2-}$ both 5×10^{-5} M. The resulting solution was left 30 min under stirring before ultrafiltration. In the subsequent ultrafiltration step, 1 ml of the solution to be filtered was left over the filter in order to avoid breaking of the membrane [25].

Stripping reactions concerning the Pd(II)/PADA system were carried out in a multi-step process (3 and in one case 4 steps). The retentate (1 ml) was mixed with 5 ml of stripping solution and the resulting mixture was stirred for 10 min before ultrafiltration. The ultrafiltration step allowed the separation of the metal-containing phase (the permeate) from the surfactant-containing phase (the retentate). In this procedure 5 ml of retentate solution were collected for each step. After each ultrafiltration experiments the membrane was immediately flushed with doubly deionized water and stored according to the method recommended by Millipore.

3. Results and discussion

3.1. Palladium

Fig. 1 shows the absorption spectra of an aqueous solution initially containing PADA 2×10^{-5} M and SDS 0.15 M (spectrum a) to which increasing amounts of $PdCl_4^{2-}$ are added up to saturation. The large spectral shift indicates that $PdCl_4^{2-}$ reacts with PADA. The absence of a single isosbestic point suggests that the binding reaction is not a single one. Actually, at the beginning of titration, i.e. under conditions of ligand excess, a complex of 1:2