

Original Paper

Study of Solid Phase Extraction Prior to Spectrophotometric Determination of Platinum with N-(3,5-Dimethylphenyl)-N'-(4-Aminobenzenesulfonate)-Thiourea

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Received July 12, 2005; accepted November 3, 2005; published online December 30, 2005

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Abstract. A highly sensitive, selective and rapid method for the determination of platinum based on the rapid reaction of platinum(IV) with N-(3,5-dimethylphenyl)-N'-(4-aminobenzenesulfonate)-thiourea (DMMPT) and the solid phase extraction of the Pt(IV)-DMMPT complex with C₁₈ membrane disks was developed. In the presence of pH = 3.8 buffer solution and cetyl trimethylammonium bromide (CTMAB) medium, DMMPT reacts with platinum to form a violet complex of a molar ratio of 1:3 (platinum to DMMPT). This complex was enriched by solid phase extraction with C₁₈ membrane disks, and an enrichment factor of 200 was obtained. The molar absorptivity of the complex is $9.51 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 755 nm, and Beer's law is obeyed in the range of 0.01–3.0 $\mu\text{g mL}^{-1}$ in the measured solution. The relative standard deviation for eleven replicate samples of 0.01 $\mu\text{g mL}^{-1}$ level is 1.79%. The detection limit reaches 0.02 $\mu\text{g L}^{-1}$ in the original samples. This method was applied to the determination of platinum in water and soil samples. The relative standard deviations are 2.9–3.4%. The recoveries are 94–105%. The values of determination obtained agree with those of the ICP-MS method. The results are satisfactory.

Key words: N-(3,5-dimethylphenyl)-N'-(4-aminobenzenesulfonate)-thiourea; platinum; spectrophotometry; solid phase extraction.

Platinum is an important element. It is important both for industry and biological systems. In rapidly expanding analytical fields such as environmental, biological and material monitoring of trace metals, there is an increasing need to develop simple, sensitive and selective analytical methods that do not use expensive or complicated test equipment [1, 3]. Many sensitive and selective instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, chemiluminescence, and the like have been widely applied to the determination of platinum [4–11]. However, the spectrophotometric methods have gained popularity because of their simplicity and low operating costs, and a wide variety of spectrophotometric methods for the determination of platinum have been reported. Each chromogenic system has its advantages and disadvantages with regard to sensitivity, selectivity and rapidity [12–19]. However, the routine spectrophotometric methods are often not sensitive enough to determine low concentrations of platinum ions in water samples or geological samples, e.g. platinum concentrations at $\mu\text{g L}^{-1}$ or ng L^{-1} level. Consequently, a preconcentration step is usually required.

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Solid phase extraction is an attractive technique because it presents notable advantages [20–24]. In this paper, based on the color reaction of *N*-(3,5-dimethylphenyl)-*N'*-(4-aminobenzenesulfonate)-thiourea (DMMPT) with platinum and combining with the solid phase extraction of the colored complex with C_{18} disks, a highly sensitive, selective and rapid method for the determination of platinum was developed.

Experimental

Apparatus

A UV-160 A spectrophotometer (Shimadzu, Japanese) equipped with a 1 cm microcell (0.5 mL) was used for all absorbance measurements. The pH values were determined with a Beckman Φ -200 pH meter. Extraction was performed on a Waters Solid Phase Extraction (SPE) device (prepares twenty samples simultaneously), and Zorbax C_{18} membrane disks [47 mm (diameter) \times 0.5 mm (thickness), 8 μ m, 50 mg] (Agilent Technologies, USA) were used.

Synthesis of DMMPT

4.8 g of 4-hydrazino-phenylsulfonic acid was placed in a three-necked flask, and the pH value was adjusted to neutral with sodium hydroxide solution. Then this solution was heated slowly in a water bath. When the temperature rose over 85 °C, an excess 3,5-dimethylphenyl-isothiocyanate alcohol solution was added. The solution immediately formed two layers. When the oil layer disappeared, the solution was allowed to stand for 1 h and subsequently left to cool to room temperature. The unreacted 3-methylphenyl-isothiocyanate was extracted by ether. The water layer was concentrated, and a precipitate was obtained. The precipitate was filtered and recrystallized 2–3 times with alcohol. A yellow powder was obtained with 54% yield. The structure was verified by elemental analysis, IR, ^1H NMR, and MS. IR (KBr, cm^{-1}): 3600 (–OH); 3460, 3300, 3180 (–N–H); 2920, 2885 (–CH₃); 1620 (C₆H₅); 1220 (–C=S); 1050 (–NHCSNH); 1180, 1125 (–Ar–SO₃). ^1H NMR: (ppm), 2.48 (6H, s, –CH₃); 7.12–7.68 (7H, m, Ar–H); 4.85 (3H, br, –NH, –NH–NH); 2.12 (1H, –OH). MS (EI) (*m/z*): 351 (*M*⁺). Elemental analysis (%): C₁₅H₁₇N₃O₃S₂, calculated (found), C 44.56 (51.26), H 4.24 (4.88), N 11.11 (11.96), S 18.12 (18.25). All these demonstrate that the structure of DMMPT has the structure shown in Fig. 1.

Reagents

All of the solutions were prepared with ultra-pure water obtained from a Milli-Q50 SP Reagent Water System (Millipore Corporation, USA). Dimethyl formamide (DMF) (Fisher Corporation, USA) was

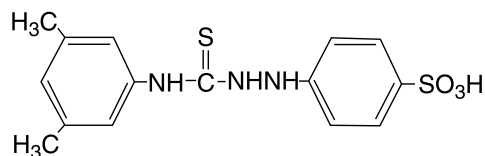


Fig. 1. Structure of DMMPT

used. DMMPT solution ($1.0 \times 10^{-3} \text{ mol L}^{-1}$) was prepared by dissolving DMMPT with water. A stock standard solution of platinum ($1000 \mu\text{g mL}^{-1}$, Pt(IV) in 10% hydrochloric acid) was obtained from the Chinese Standard Center, and the working solutions used were prepared by diluting this solution. The buffer solution of 0.5 mol L^{-1} acetic acid–sodium acetate was prepared by dissolving 30 g acetic acid in 600 mL of water, then adjusting the pH to 3.8 with sodium hydroxide solution and diluting to a volume of 1000 mL with water. The Cetyl trimethylammonium bromide (CTMAB) solution (1.0%) was prepared by dissolving CTMAB with 10% ethanol. All chemicals used were of analytical grade unless otherwise stated.

General Procedure

To a standard or sample solution containing no more than 3.0 μg of Pt(IV) in a 200 mL calibrated flask, 10 mL of 0.5 mol L^{-1} acetic acid–sodium acetate buffer solution with pH 3.8, 6 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ DMMPT solution and 5.0 mL of 1.0% CTMAB solution were added. The mixture was diluted to the volume of 200 mL and mixed well. After 10 min, the solution was passed through the C_{18} disks at a flow rate of 50 mL min^{-1} . After enrichment was complete, the retained complexes were eluted from the disks with 1.0 mL of DMF at a flow rate of 5 mL min^{-1} . The absorbance of the eluent was measured in a 1 cm cell at 755 nm against a reagent blank prepared in a similar way without platinum.

ICP-MS Analysis

The ICP-MS analysis was carried out on a VG Plasma Quad PQ-3 ICP-MS instrument (Micromass Corporation, UK) as described in the literature [25]. The operating conditions were as follows: frequency (MHz) 40.68; R.F. power (KW) 1.2; sampling depth (mm) 12; carrier flow (L min^{-1}); dwell time (ms) 100; replicate accumulation 20; channel width 3; replicate measurements 3.

Before all analyses, the instrument was checked for mass calibration response curve, resolution, oxide and double charge ion formation in accordance with the manufacturer's guidelines. In the conventional ICP-MS procedure, In and Re were used as internal standards to monitor and correct for any suppression of the signal due to matrix effects.

Results and Discussion

Optimization of Spectrophotometric Determination

The absorption spectra of DMMPT and its Pt(IV) complex are shown in Fig. 2. The absorption peak of DMMPT is at 248 nm. The absorption peaks of DMMPT–Pt(IV) complex in DMF medium are located at 336 nm ($\epsilon 13.5 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 755 nm ($\epsilon 9.51 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). However, at 755 nm, some metal–DMMPT complexes, such Pd, Cu, Au, Pb, Ag have very low absorbance and do not interfere with the platinum determination. Considering the selectivity, the determining wavelength is selected at 755 nm.

The results showed that the optimal pH for the reaction of Pt(IV) with DMMPT is 1.5–5.8. A pH

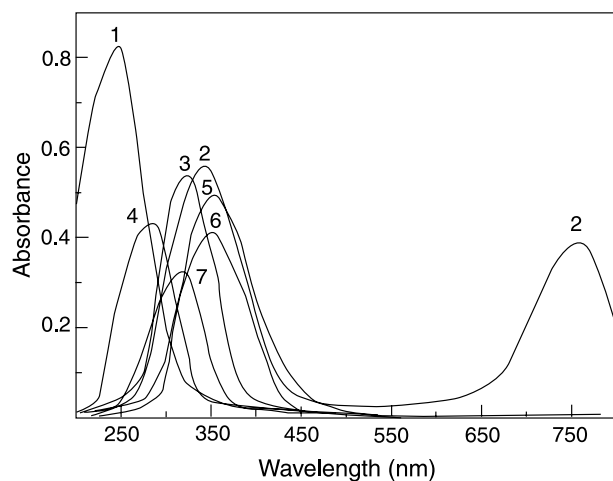


Fig. 2. Absorption spectra of DMMPT and its metal chelate (1) DMMPT blank; (2) Pt-DMMPT; (3) Pd-DMMPT; (4) Pb-DMMPT; (5) Au-DMMPT; (6) Cu-DMMPT; (7) Ag-DMMPT

3.8 acetic acid–sodium acetate buffer solution was recommended to control the pH.

The effects of routine surfactants including Tween-20, Tween-80, emulsifier-OP, PVA, SLS, AG, Triton X-100, CTMAB, and CPB on the Pt-DMMPT complex were tested. None of them increases the absorbance markedly. However, the retention of Pt-DMMPT complex on the C_{18} disks was greatly increased when 3.0–8.0 mL of 1.0% CTMAB solution was used, and 5.0 mL was recommended for all further experiments.

For up to 3.0 μg of Pt(IV), the use of about 5–10 mL of $1.0 \times 10^{-3} \text{ mol L}^{-1}$ DMMPT solution was found to be sufficient for complete reaction, and 6 mL of DMMPT solution was added for all further experiments.

After mixing the components, the absorbance reaches its maximum within 6 min at room temperature and remains stable for 6 h in aqueous solution. The complexes are stable for at least 20 h when extracted into the DMF medium.

Solid Phase Extraction

Both enrichment and elution were carried out on a Waters SPE device (prepares twenty samples simultaneously). The flow rate was set to 50 mL min^{-1} for enrichment and 5 mL min^{-1} for elution.

Some experiments were carried out in order to investigate the retention of DMMPT and its Pt(IV) complex on the disks. It was found that the DMMPT and its Pt(IV) complex were retained on the disks quantitatively when they pass the disks as aqueous

solution. The capacity of the disks for the Pt(IV)-DMMPT complex was determined as 22 mg in 200 mL of solution. In this experiment, the disks have adequate capacity to enrich the Pt(IV)-DMMPT complex.

In order to choose a suitable eluent for the retained DMMPT and its Pt(IV) complex, various organic solvents were studied. The volume of the solvent needed is 0.8 mL for DMF, 1.2 mL for isopentyl alcohol, 1.4 mL for acetone, 1.4 mL for acetonitrile, 1.8 mL for ethanol, 2.0 mL for methanol. Maximum enrichment was achieved when DMF was selected as eluent. So DMF was selected as eluent. The experiment showed that it was easier to elute the retained DMMPT and its Pt(IV) complex in reverse direction than in forward direction (only 0.8 mL of eluent is needed when eluting in reverse direction; however, 2.2 mL of eluent is needed when eluting in forward direction). Therefore, it is necessary to upturn the disks for elution. 1.0 mL of DMF was sufficient to elute the DMMPT and its Pt(IV) complex from the disks at a flow rate of 5 mL min^{-1} . A volume of 1.0 mL DMF was selected.

Calibration Curve and Sensitivity

The calibration curve shows that Beer's law is obeyed in the concentration range of 0.01–3.0 $\mu\text{g Pt(IV)}$ per mL in the measured solution. The linear regression equation obtained was: $A = 0.485 C (\mu\text{g mL}^{-1}) + 0.0228$, ($r = 0.9993$). The molar absorptivity was calculated to be $9.51 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ at 755 nm. The relative standard deviation at a concentration level of 0.02 $\mu\text{g Pt(IV)}$ per mL (11 replicate determinations) was 1.79%.

Table 1. Tolerance limits in the determination of 0.005 $\mu\text{g mL}^{-1}$ of Pt with DMMPT (relative error $\pm 5\%$)

Ion added	Tolerated ($\mu\text{g mL}^{-1}$)
NO_3^- , Cl^- , Na^+ , K^+ , borate	250
oxalate, citrate, benzoate, succinate, ascorbate, SO_4^{2-} , NH_4^+	100
Li^+ , Al^{3+} , PO_4^{3-} , tartrate	50
F^- , Br^- , ClO_4^- , I^- , Ca^{2+} , Mg^{2+}	25
Sr^{2+} , Ce(IV) , Ba^{2+} , Zr(IV) , Zn^{2+} , Fe^{3+}	10
Mn^{2+} , W(VI) , Mo(VI) , Cu^{2+}	5
Ti(IV) , Bi(III) , V(V) , Cr(VI) , Zr(IV) , Ni^{2+} , Th(IV)	2.5
Tl(III) , Ag^+ , Cd^{2+} , Cr^{3+} , Fe^{2+} , La^{3+} , Sn(IV) , Rh^{3+} , Pb^{2+}	1.5
Ru(III) , Bi(III) , Hg^{2+} , Sb^{3+} , Pd^{2+} , Sn(IV) , Sb(III) , Co^{2+}	1.0
SCN^- , Se(IV) , U(VI) , Te(IV) , Au^{3+}	0.5

Table 2. Determination of platinum in water and soil samples

Samples	Found	ICP-MS method	RSD% (n = 5)	Recovery (%) (n = 5)
River water	12.8 ($\mu\text{g L}^{-1}$)	11.6 ($\mu\text{g L}^{-1}$)	3.2	92–98
Plant effluents	33.1 ($\mu\text{g L}^{-1}$)	31.5 ($\mu\text{g L}^{-1}$)	2.9	94–105
Soil (vicinity of highway)	112 (ng g^{-1})	121 (ng g^{-1})	3.2	95–104
Soil (general)	26.7 (ng g^{-1})	25.6 (ng g^{-1})	3.4	90–97

Composition of the Complex

The composition of the complex was determined by continuous variation and the molar ratio method. Both showed that the molar ratio of Pt(IV) to DMMPT is 1:3.

Interference

The selectivity of the proposed method was investigated by the determination $0.005 \mu\text{g mL}^{-1}$ of Pt(IV) in the presence of various ions within a relative error of $\pm 5\%$. The tolerance limits are given in Table 1. Results show that this method is high selectivity.

Application

For water samples, the samples were acidified with hydrochloric acid and filtered through an $0.45 \mu\text{m}$ filter. Then the platinum contents were analyzed according to the general procedure. The recovery test for platinum was performed by adding $0.2 \mu\text{g}$ of Pt(IV) to the sample according to the standard addition procedure. The results (deducting the reagents blank) are shown in Table 2. An ICP-MS method was used as a reference method, the results of which are also shown in Table 2.

For soil samples, a 5.0 g soil sample is weighed into a 250 mL Teflon high-pressure microwave acid-digestion bomb (Fei Yue Analytical Instrument Factory, Shanghai, China), to which 50 mL of aqua regia was added. The bombs were sealed tightly and then positioned into the carousel of the microwave oven (Model WL 5001, 1000 W, Fei Yue Analytical Instrument Factory, Shanghai, China). The system was operated at full power for 30 min. The digested material was evaporated to incipient dryness. Then 50 mL of 5% hydrochloric acid was added and heated close to boiling to leach the residue. After cooling, the residue was filtrated, and the undissolved residue was washed with 5% hydrochloric acid twice. The leachate was collected in a 200 mL calibrated flask

quantitatively before the platinum contents were analyzed according to the general procedure. The recovery test for platinum was performed by adding $0.2 \mu\text{g}$ of Pt(IV) to the sample according to the standard addition procedure. The results (deducting the reagents blank) are also shown in Table 2. An ICP-MS method was used as a reference method, the results of which are also shown in Table 2.

Conclusion

The proposed method has the following characteristics: (1) DMMPT is a highly sensitive and selective reagent. The molar absorptivity of the Pt(IV)-DMMPT-CTMAB complex reaches $9.51 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ in the measured solution, and most foreign ions do not interfere with the determination. (2) By solid phase extraction with C_{18} disks, an enrichment factor of 200 was achieved. The detection limit reaches $0.02 \mu\text{g L}^{-1}$ in the original samples, and low concentrations of platinum in samples can be determined with good results. (3) Using a Waters SPE device, twenty samples can be prepared simultaneously. This method is suitable for simultaneously preparing large amounts of sample within a short time.

Acknowledgement. This work was supported by the National Natural Science Foundation of China (20471051) and the Key Natural Science Foundation of Yunnan Province (2005K021).

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