

Column preconcentration of palladium using protocatechuic acid and tetradecyldimethylbenzylammonium-iodide-naphthalene as an adsorbent

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A preconcentration procedure has been established for the determination of trace amounts of palladium with a solid ion-pair of tetradecyldimethylbenzylammonium (TDBA) and iodide on microcrystalline naphthalene using a simple funnel-tipped glass tube as the preconcentration column. Palladium reacts with protocatechuic acid to form a water-soluble coloured complex anion. The complex anion forms a water-insoluble palladium-protocatechuic acid-TDBA complex on naphthalene packed in a column. Palladium is quantitatively retained on the naphthalene in the pH range 4.0-7.0 and at a flow rate of 2 ml/min. The solid mass consisting of palladium complex and naphthalene is washed from the column with 5 ml of dimethylformamide (DMF) and trace amounts of palladium measured by atomic absorption spectrometry at 244.8 nm. The detection limit is 0.0257 µg/ml. The developed method has been tested for the determination of palladium in synthetic as well as actual samples.

Some metal ions may be preconcentrated using some adsorbents such as green tea leaves¹, chelating resin², silica gel³, thiol cotton⁴ and polyurethane foam⁵. Some of these are fairly effective but their preparations are sometimes cumbersome and the desorption of metal chelate involves the slow process of elution.

In the present note, an efficient method of preconcentration and separation of Pd is reported using an ion pair adsorbent composed of I⁻ and TDBA⁺ supported on naphthalene. The metal is determined directly by AAS method and conditions have been developed for the determination of palladium in synthetic and actual samples. The newly developed method is economical, rapid and sensitive.

Experimental

A standard palladium solution (5 ppm) was pre-

pared by diluting 1000 ppm standard palladium chloride (Wako Pure Chemical Industries Ltd, Japan) with doubly distilled water. A 0.5% solution of protocatechuic acid was prepared in distilled water. Buffer solutions of pH 8-11 and 3-6 were prepared by mixing 0.5 M aqueous ammonia/0.5 M ammonium acetate and 0.5 M acetic acid/0.5 M ammonium acetate respectively in appropriate volumes using a pH meter⁶. A Perkin-Elmer model 403 atomic absorption spectrometer fitted with a palladium hollow cathode lamp and a Toa-Dempa HM-5A pH meter were used. A funnel-tipped glass tube (50 × 6 mm i.d.) was used as a preconcentration column. The column was plugged with coarse polypropylene fibres and packed with naphthalene to a height of 1.0-1.5 cm.

Preparation of TDBA-I-naphthalene adsorbent

A solution of naphthalene was prepared by dissolving 20 g of naphthalene in 40 ml of acetone on a stirring-hot plate system at 35°C. The solution was transferred to 1500 ml of water containing 3.5 g of potassium iodide with constant stirring, and then to it was slowly added a solution of TDBA (1.5 g) in 500 ml water. The naphthalene mixture, coprecipitated with TDBA and iodide ions was stirred for 3 hr and allowed to stand for 2 hr. The supernatant solution was drained off by decantation and the mixture was washed twice with water. The slurry of naphthalene in water was stored in a brown bottle.

General procedure

An aliquot of palladium solution (0.5-35 µg of palladium) was taken in a 20-ml beaker and to it were added 0.8 ml of 0.5% protocatechuic acid and 0.5 ml of the buffer (pH 5.5). The solution was diluted to 20 ml with water. This solution was passed through a column packed with naphthalene-I-TDBA adsorbent at a flow rate of 2 ml/min. The packing was washed with small volumes of water and aspirated for a few minutes while pushing with a flatted glass rod. The metal complex along with the naphthalene was stripped with 5 ml of DMF from the column. This solution was aspirated into an air/acetylene flame and the absorbance was measured at 244.8 nm against the reagent blank.

Results and discussion

The optimum conditions were established by taking 15 µg of palladium. The retention of palladium on this adsorbent was found to be constant and

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maximum in the pH range 4.0-7.0. All the experiments were carried out at pH 5.5. The addition of 0.5-3.0 ml of the acetate buffer did not affect the retention but the use of 0.5 ml buffer is recommended. The flow rate was varied from 1-20 ml/min and it was observed that 2 ml/min was the optimum flow rate. The percent retention of palladium on this adsorbent remained constant when the volume of the aqueous phase did not exceed 160 ml. In all the subsequent experiments 20 ml of the aqueous solution was used for convenience. Different volumes (0.1-2.0 ml) of 0.5% protocatechuic acid solution were used. The retention of palladium remained constant when 0.2 ml of this reagent was used, but a volume of 0.8 ml is recommended.

Various solvents were tried to dissolve the naphthalene-Pd-protocatechuic acid-TDBA complex from the column. The solid material is insoluble in common organic solvents such as toluene, 1,2-dichloroethane, nitrobenzene, methyl isobutyl ketone, chloroform, diethyl ether, *o*-dichlorobenzene, tri-*n*-butyl phosphate, benzene, xylene, carbon tetrachloride, but soluble in methyl alcohol, ethyl alcohol, *n*-butyl alcohol, *n*-amyl alcohol, iso-amyl alcohol, 1,4-dioxane, acetonitrile, DMSO, acetone and DMF. DMF was found to be the most suitable solvent.

It was found that 5 ml of this solvent was sufficient to dissolve the mixture. Since only a small volume of the solvent is required to dissolve the complex and naphthalene, it is essential to study the effect of the surplus water attached to naphthalene. It was found that the surplus water decreased the absorbance by 10% leading to an error in the determination. Thus,

it is necessary to eliminate the water attached to naphthalene in the column by aspirating it.

Based on the optimum conditions described above, a calibration curve was plotted over the concentration range 0.5-35.0 μg of palladium (0.1-7.0 ppm) in 5 ml of the DMF solution. Seven replicate determinations of 15 μg of palladium gave a mean absorbance of 0.106 with a relative standard deviation of 0.7%. The detection limit was 0.0257 $\mu\text{g}/\text{ml}$ ^{7,8}.

Effect of diverse ions

Sample solutions containing 15 μg of palladium and various amounts of diverse ions were prepared and analyzed by the general procedure. The following (amount shown in parentheses) ions did not interfere. Sodium acetate (100 mg), NH_4Cl , Na_2SO_4 (30 mg each), KNO_3 (20 mg), $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ (15 mg), KCN, Na, K tartrate, KH_2PO_4 , H_2O_2 (5 mg each), ammonium citrate, $\text{Na}_2\text{C}_2\text{O}_4$ (3 mg each), NaCl, NH_4F , $\text{Na}_2\text{S}_2\text{O}_3$ (2 mg each), NaClO_4 , H_2O , NH_4SCN (1 mg each), KI, EDTA (10 μg each) and EGTA (5 μg). Among the cations examined, Ca^{2+} , W^{6+} , Mg^{2+} (1 mg each), Cr^{6+} , Ni^{2+} (800 μg each), Ag^+ (150 μg , 800 μg after masking with 2 mg of $\text{Na}_2\text{S}_2\text{O}_3$), Mo^{6+} , Cd^{2+} , Cu^{2+} (500 μg each), Co^{2+} , (400 μg), Pb^{2+} , Pt^{4+} , Au^{3+} (300 μg each), Zn^{2+} , Hg^{2+} (200 μg each), Bi^{3+} , Al^{3+} (150 μg each), V^{5+} , Ru^{3+} , Mn^{2+} (100 μg each), Fe^{3+} (50 μg , 100 μg after masking with 2 mg of $\text{Na}_2\text{C}_2\text{O}_4$), Fe^{2+} (3 μg , 100 μg after masking with 2 mg of $\text{Na}_2\text{C}_2\text{O}_4$) and Cr^{3+} (3 μg , 100 μg after masking with 2 ml of 30% H_2O_2) did not show any interference. Thus the method is fairly selective and can be applied for the determi-

Table 1—Determination of palladium in synthetic and real samples

Composition of sample (%)	Palladium taken (μg)	Palladium found (μg)	Average value (μg)	Recovery (%)
Pt-Pd-Au (20:20:60)	12.00	12.21, 12.00 11.80, 12.00	12.00	100.0
Ag-Pd (80:20)	30.00	29.86, 30.28 31.13, 30.00	30.31	101.0 ^a
Co-Pd (95:5)	30.00	29.14, 29.71 30.00, 29.43	29.57	98.6 ^b
Ni-Pt-V-Pd (60:20:9.5:10.5)	12.00	11.75, 12.25 11.63, 11.76	11.85	98.8
Ni-Pt-V-Pd (60:30:7:2.5)	6.00	6.00, 5.91 6.09, 5.83	5.96	99.3
Pd/alumina 5.12% (by direct AAS method)	—	5.67 $\pm$ 0.09	—	—
Pd asbestos 9.89% (by direct AAS method)	—	10.11 $\pm$ 0.13	—	—

0.5% protocatechuic acid: 0.8 ml; pH: 5.5; Wavelength: 244.8 nm.

^amasked with 2 mg of $\text{Na}_2\text{S}_2\text{O}_3$.

^bmasked with 1 mg of potassium sodium tartrate.

nation of palladium in synthetic and real samples (Pd/alumina and Pd/asbestos).

The developed method has been tested for the synthetic mixtures corresponding to the standard alloys of palladium reported in the literature⁹. The synthetic mixtures containing various metal ions listed in Table 1 were prepared and the general procedure of estimation was followed. A 10 mg amount of Pd/alumina was completely dissolved in 5 ml of conc. HNO_3 and 2 ml of HClO_4 on a water-bath. The mixture was evaporated to dryness and dissolved in 1 ml of 1 N HNO_3 and 10 ml of water. This was filtered and the volume made up to 100 ml in a flask. A sample of palladium asbestos (10 mg) was ashed in a crucible, dissolved in 5 ml of aqua regia on a water-bath and evaporated to dryness. The residue was dissolved in 3 ml of conc. HNO_3 and evaporated to dryness. This was dissolved in water containing 2 ml of 0.5 N HNO_3 , filtered and diluted to 100 ml with water in a standard flask. An aliquot (1 ~ 2 ml) of the sample solution was taken in a beaker and similar procedure was followed.

Thus it is observed that use of the ion-pair material produced from iodide and TDBA on naphthalene provides a simple, rapid and economical method for the column preconcentration of palladium in samples. The proposed method is the first attempt to separate palladium using the reaction of

Pd-protocatechuic acid complex anion with the quaternary ammonium cation. The solvent extraction gives a simple and efficient separation procedure, but it is difficult to extract some metals in the presence of surfactants because of the emulsion formation in two phases on shaking. In such a case, larger amounts of salting-out agent must be added in the solution for the phase separation of the complex. The proposed method has proved to be effective for the analysis of trace amounts of palladium in synthetic and real samples. There is no need of regeneration of the adsorbent as needed in ion exchange and Chelex-100 methods. The sensitivity of the method may be improved further by using other optical analytical techniques of analysis like graphite furnace AAS.

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