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The Sensitive and Selective Determination of Palladium(II) Based on Ternary-Complex Formation with Phloxine and Thiamine[1)]

Yoshikazu FUJITA, Itsuo MORI,* Minako TOYODA, Yoshihiro NAKAHASHI, Keiji KATO, and Masaki NAKAMURA
Osaka University of Pharmaceutical Sciences, 2-10-65, Kawai, Matsubara-shi, Osaka 580

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A sensitive and selective spectrophotometric determination of palladium(II) based on ternary-complex formation with Phloxine and thiamine was established. The apparent molar absorptivity of the proposed method, which does not require an extraction procedure, was 1.02×10^5 dm^3 mol^{-1} cm^{-1} at 565 nm. Only gold(III) in an equimolar ratio of palladium(II) among the metal ion examined interfered. The method was applied to a determination of palladium in palladium carbon and palladium asbestos; the results were in good agreement with those obtained by potassium iodide method, the Michler's thioketone method and ICP-AES. The sensitivity could be further enhanced by about 20 times over that of spectrophotometry and/or fluorimetry by combining it with a membrane filter preconcentration technique. It was suggested that the collection of an aggregate on a membrane filter depends on the molecular size through observing by an scanning electron microscope.

Various determination methods for metal ions based on the ternary-complex formation have been reported[2—4)] for the purpose of enhancing the determination sensitivity, selectivity and so on. Of the ternary-complex system, the ion-association type based on complex formation between a metal ion-organic base cation and the anion of a dyestuff has often used. The organic bases used are limited[3,4)] to such ligands as 1,10-phenanthroline and 2,2′-bipyridyl. Most of these methods are not sufficiently selective and require an extraction step in spite of the high sensitivity.

We have already reported[5—7)] on the determination of organic compounds utilizing a ternary-complex system, {**RML**}, where {**R**}, {**M**}, and {**L**} denote an organic dye, a metal ion and an organic compound, respectively. In previous papers[6,7)] a simple and sensitive determination of {**L**}, such as thiamine and chlorpromazine, was established by using {**RML**} with Eosine, palladium(II) and these {**L**}. In this case only palladium(II) was effective among the various metal ions tested. Thus, it is speculated that a simple, sensitive and selective determination of palladium(II) would be established by selecting suitable {**R**} and/or {**L**}, particularly {**L**}.

We studied the color reactions of palladium(II) based on the formation of a new type of the ternary complex with fluorescein(fl) dyes, palladium(II) and {**L**}; a selective and sensitive determination of palladium(II) was investigated by using Phloxine as {**R**} and thiamine as {**L**}. The proposed method was applied to an assay of palladium in practical samples. In addition, a membrane filter preconcentration technique[8,9)] was also studied for the purpose of enhancing the determination sensitivity. A collection of ternary-complex aggregates on a membrane filter was observed with a scanning electron microscope (SEM).

Experimental

Apparatus. The absorption spectra and absorbance values were measured with a Shimadzu Model 160 recording spectrophotometer using 1.0-cm quartz cells. A Shimadzu Model RF-540 spectrofluorometer with a 1.0-cm quartz cell was used. The pH measurements were made with a Hidachi-Horiba F-7 AD glass electrode pH meter. A Shimadzu Model ICPS-1000V inductively coupled plasma emission spectrometer was used. A Toyo TM 3 membrane filter(made of nitrocellulose, 25 mm diameter, 0.65 μm pore size) and Toyo KGS-25 filter holder were used.

Reagents and Materials. A stock solution (1.0×10^{-2} mol dm^{-3}) and a working solution of palladium(II) were prepared according to a previous report.[7)] All fl derivative solutions were prepared in 1.0×10^{-3} mol dm^{-3} aqueous solutions. 2,4,5,7-Tetrabromo-3′,4′,5′,6′-tetrachloro fl (Phloxine), 2,4,5,7-tetrabromo fl (Eosine), 2,4,5,7-tetraiodo-3′,4′,5′,6′-tetrachloro fl (Rose Bengal), 2,4,5,7-tetraiodo fl (Erythrosine), 4,5-dibromo fl and 4,5-diiodo fl were purchased from Wako Pure Chemical Ind. Ltd., Tokyo Kasei Kogyo Co., Ltd., and Aldrich Chemical Com. Inc., respectively. Fl, 2,4,5,7-tetrachloro fl, 2,7-dichloro fl and 3′,4′,5′,6′-tetrachloro fl were synthesized according to methods described in the literature.[10,11)] A 5.0×10^{-3} mol dm^{-3} thiamine solution was prepared by dissolving thiamine hydrochloride in water. A 1.0% aqueous solution of (2-hydroxypropyl)cellulose (HPC, 6-10 cps) and polyethylene glycol (PEG, 2000) were prepared. A 0.2 mol dm^{-3} sodium acetate-0.2 mol dm^{-3} acetic acid buffer solution was used for pH adjustments. All other reagents and materials were of analytical reagent grade, and deionized water was used.

Standard Procedure for the Spectrophotometry. To a solution containing up to 8 μg of palladium(II) were added 0.3 cm^3 of a 5.0×10^{-3} mol dm^{-3} thiamine solution, 0.5 cm^3 of a 1.0% HPC solution, 3.0 cm^3 of the buffer solution (pH 4.6) and 1.0 cm^3 of a 1.0×10^{-3} mol dm^{-3} Phloxine solution; the solution was diluted to mark with water in a 10-cm^3 volumetric flask. After being kept at room temperature for 20 min, the absorbance of a Phloxine-thiamine-palladium(II) solution (Solution A) was measured at 565 nm against the Phloxine-thiamine (=reagent blank, Solution B) as a reference.

Recommended Procedure for a Membrane Filter Preconcentration. A solution containing up to 0.5 μg of palladium(II) was placed in a 10-cm^3 volumetric flask; to this were added 0.3 cm^3 of a 5.0×10^{-3} mol dm^{-3} thiamine solution, 0.3 cm^3 of a 1.0 % PEG solution, 3.0 cm^3 of the buffer solution (pH 4.6), and 1.0 cm^3 of a 1.0×10^{-3} mol dm^{-3} Phloxine solution. The mixture was diluted to the mark with water, agitated well, and kept at room temperature for 20 min together with a reagent blank. Both solutions were then filtered through a 0.65-μm pore size membrane filter to collect the aggregates; the filtered substances were then washed with about 20 cm^3 of water. After being dried with a hair-drier, the membrane filter and aggregates were dissolved in 5 cm^3 of dimethyl sulfoxide (DMSO). The absorbance of a DMSO solution containing palladium(II) (Solution A′) was measured at 555 nm against the DMSO solution of a reagent blank (Solution B′). In the case of fluorimetry, the difference in the relative fluoresence intensity between Solutions A′ and B′ at 575 nm emission wavelength with excitation at 520 nm was measured.

Results and Discussion

Choice of Dye {R} and Organic Base {L}. In order to examine the effect of {R} on the color reaction among {R}, {L} and palladium(II), thiamine was selected as {L}. In the absence of a dispersion agent Solution A precipitated gradually; thus, a nonionic surfactant,[9] such as HPC and Methyl Cellulose, was added to Solutions A and B. Of the ten fl derivatives tested, Phloxine, Eosine, Erythrosine, and Rose Bengal were superior to the other {R} in sensitivity. The relationships between the pH change and absorbance by using these four {R} are shown in Fig. 1.

The effect of {L} was examined by combinations of four {R} and various {L} at each optimum pH. Of the various {L} examined (thiamine, papaverine, dibucaine, scopolamine, pilocarpine, pyridoxine, lincomycin, quinine, ergotamine, chlorpromazine, chlorhexidine, acrinol, theophylline, cycloserine, diphenhydramine, sparteine, and spermine), thiamine was the best since it gave the highest sensitivity and stability of the coloration. In addition, compared with the other {R}, thiamine scarcely produced the colored complex with {R}, i.e. the absorbance of Solution B was relatively low. {R} could be arranged in the following order with respect to sensitivity: Phloxine≈Rose Bengal>Erythrosine≈Eosine. Phloxine was superior to Rose Bengal in terms of color contrast between sample and reagent blank solutions, and the purity of reagent. The results are shown in Table 1.

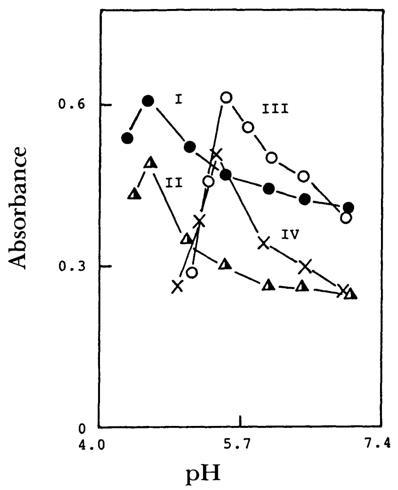

Fig. 1. Effect of pH on the color reaction between palladium(II) and dye-thiamine solution.
Pd(II): 6.0×10^{-6} mol dm^{-3} (4.2 μg/10 cm^3); dye: 1.0×10^{-4} mol dm^{-3}; thiamine: 1.5×10^{-4} mol dm^{-3}; HPC: 0.05%; Reference: Solution B (dye-thiamine solution); dye: I (—●—), Phloxine; II(—▲—), Eosine; III (—○—), Rose Bengal; IV (—X—), Erythrosine.

On the basis of these resutls, Phloxine and thiamine were chosen as {R} and {L}, respectively, for the further experiments.

Optimisation of Conditions. The maximum difference in absorbance between Solutions A and B was at 565 nm. The optimum pH for the color reaction was narrow and was 4.5—4.7. The absorbance of Solution A against Solution B dropped rapidly at both higher and lower pH regions. Hence, 3.0 cm^3 of 0.2 mol dm^{-3} acetate buffer solution (pH 4.6) was used for the pH adjustments. Of various nonionic surfactants tested (HPC, Methyl Cellulose, PEG, poly(*N*-vinylpyrrolidone) and poly(vinyl alcohol)), HPC was the

Table 1. Effect of Organic Bases {L} by Using Four fl Dyes {R}

{L}	{R}, Absorbance at (λ/nm)			
	Phloxine	Eosine	Rose Bengal	Erythrosine
Thiamine	0.610 (565)	0.510 (545)	0.615 (580)	0.502 (560)
Papaverine	0.134[a)] (575)	0.153[a)] (540)	0.103[a)] (565)	0.095[a)] (560)
Dibucaine	0.153[a)] (575)	0.097[a)] (540)	0.102[a)] (565)	0.079[a)] (560)
Scopolamine	0.089[a)] (545)	0.072 (540)	0.096[a)] (565)	0.096[a)] (535)
Pilocarpine	0.144 (565)	0.079 (540)	0.276 (575)	0.099[a)] (535)

Pd(II): 6.0×10^{-6} mol dm^{-3}; {R}: 1.5×10^{-4} mol dm^{-3}; HPC: 0.05%; pH: Phloxine and Eosine—pH 4.5, Rose Bengal and Erythrosine—pH 5.5; Reference: {L}-{R} solution (Solution B).
a) {R-L} complex produced and absorbance of {L}-{R} solution was remarkably high.

best in terms of sensitivity and stability of coloration. A constant absorbance was obtained by the addition of more than 0.1 cm^3 of 1.0% HPC solution to the final volume of 10 cm^3. Since a maximum and almost constant absorbance was obtained upon by the addition of more than 0.2 cm^3 of 5.0×10^{-3} mol dm^{-3} thiamine solution, 0.3 cm^3 was adopted in the final volume of 10 cm^3. Further experiments were carried out with 1.0×10^{-4} mol dm^{-3} Phloxine in the final volume, considering the absorbance of Solution B.

Under standard conditions, the constant absorbance of Solution A at 565 nm against Solution B as a reference was obtained by maintaining it at room temperature for more than 15 min; the absorbance value was almost constant for at least 3 h. Therefore, 20 min of standing time at room temperature was adopted for all measurements.

Calibration Curve. Beer's law held over the range up to 8 μg of palladium(II) in the final volume of 10 cm^3. The apparent molar absorptivity (ε) and the Sandell sensitivity were 1.02×10^5 dm^3 mol^{-1} cm^{-1} and 0.0010 μg cm^{-2}, respectively. This procedure is much more than the methods using potassium iodide[12] (KI, $\varepsilon=1.02\times10^4$) and dithizone[13] ($\varepsilon=3.55\times10^4$), but less sensitive than the methods using Michler's thioketone[14] (MTK, $\varepsilon=3.0\times10^5$) and Rhodamine 6G[15]

Table 2. Effect of Foreign Ions

Ions	Added as	Added (μg/10 cm^3)	Added Mole ratio[a)]	Absorbance at 565 nm	Recovery %
—	—	—	—	0.408	100.0
Fe(III)	Alum	4.5×10	20	0.414	101.5
Au(III)	$HAuCl_4$	3.9	1/2	0.477	116.9
Rh(III)	$RhCl_3$	4.1×10^2	100	0.408	100.0
Ir(III)	$IrCl_3$	3.8×10	5	0.385	94.4
Ru(III)	$RuCl_3$	4.0×10	10	0.415	101.8
Sc(III)	$ScCl_3$	3.6×10	20	0.408	100.0
Al(III)	$AlCl_3$	5.4×10	50	0.408	100.0
La(III)	$LaCl_3$	5.6×10^2	100	0.408	100.0
Bi(III)	$Bi(NO_3)_3$	8.4×10	10	0.423	103.7
Ti(IV)	$Ti(SO_4)_2$	3.8×10	20	0.402	98.5
Pt(IV)	$PtCl_4$	1.6×10^2	20	0.392	96.1
Zr(IV)	$Zr(NO_3)_4$	1.8×10	5	0.425	104.2
V(V)	NH_4VO_3	2.0×10	10	0.394	96.6
Ta(V)	TaF_5	3.6×10^2	50	0.402	98.5
Mo(VI)	Na_2MoO_4	3.8×10	10	0.392	96.1
Cr(VI)	K_2CrO_4	2.1×10^2	100	0.408	100.0
Re(VII)	$HReO_4$	7.4×10^2	50	0.395	96.8
Os(VIII)	OsO_4	3.8×10	5	0.396	97.1
Cu(II)	$Cu(NO_3)_2$	1.3×10^2	50	0.408	100.0
Co(II)	$Co(NO_3)_2$	1.2×10^2	50	0.408	100.0
Ni(II)	$Ni(NO_3)_2$	1.2×10^2	50	0.408	100.0
Cd(II)	$Cd(NO_3)_2$	4.5×10^2	100	0.408	100.0
Hg(II)	$Hg(NO_3)_2$	1.6×10^2	20	0.432	105.9
Mn(II)	$MnCl_2$	2.2×10^2	100	0.408	100.0
Zn(II)	$ZnCl_2$	2.6×10^2	100	0.408	100.0
Pb(II)	$PbCl_2$	8.3×10^2	100	0.408	100.0
Mg(II)	$MgCl_2$	9.7×10	100	0.408	100.0
Ag(I)	$AgNO_3$	2.2×10^2	20	0.433	106.1
Cl^-	NaCl	3.5×10^2	250	0.408	100.0
Br^-	KBr	8.0×10^2	250	0.385	94.4
I^-	KI	1.0	1/5	0.382	93.6
S^{2-}	Na_2S	1.3×10^{-1}	1/10	0.358	87.7
$S_2O_3^{2-}$	$Na_2S_2O_3$	4.5×10^{-1}	1/10	0.347	85.0
SO_3^{2-}	Na_2SO_3	6.4×10^{-1}	1/5	0.384	94.1
SCN^-	NH_4SCN	5.8×10^{-1}	1/4	0.357	87.5
CN^-	KCN	2.1×10^{-1}	1/5	0.359	88.0
NO_2^-	$NaNO_2$	9.2×10^{-1}	1/2	0.394	99.6
F^-	KF	7.6×10	100	0.408	100.0
PO_4^{3-}	KH_2PO_4	3.8×10^2	100	0.408	100.0
SO_4^{2-}	K_2SO_4	9.6×10^2	250	0.408	100.0
$C_2O_4^{2-}$	$Na_2C_2O_4$	3.5×10	10	0.368	90.2
Tartrate	Sodium tartrate	5.9×10^2	100	0.408	100.0
Citrate	Sodium citrate	7.6×10^2	100	0.408	100.0

Pd(II) taken: 4.2 μg/10 cm^3; Phloxine: 1.0×10^{-4} mol dm^{-3}; HPC: 0.05%; pH: 4.6; Reference: Solution B. a) Ion/Pd(II).

($\varepsilon=3.0\times10^5$).

The relative standard deviation (R.S.D.) was 0.84% for ten runs with 4.2 μg of palladium(II).

Interference. Various amounts of foreign metal ions were added to a fixed amount of palladium(II) (4.2 μg). There was no interference under the following conditions: 50- to 100-fold molar ratio of copper(II), cobalt(II), nickel(II), cadmium(II), zinc(II), lead(II), manganese(II), lanthanum(III), chromium(III); 10- to 20-fold molar ratio of titanium(IV), iron(III), mercury(II), scandium(III), rhodium(III), silver(I); equimolar to 2-fold molar ratio of molybdenum(VI), bismuth(III), zirconium(IV), osmium(VIII), iridium(III). Only gold interfered in equimolar ratio of palladium(II). On the other hand, among the anions tested, chloride, sulfate, phosphate, citrate, tartrate, nitrate, and fluoride ions did not interfere in 100- to 250-fold excess over palladium(II). A fairly large error appeared in the presence of some anions belonging to soft bases (sulfide, thiosulfate, nitrite, cyanide, and iodide ions) at a low concentration because of a complex formation between these anions and palladium(II). Interference from gold(III) up to a 2-fold molar ratio of palladium(II) could be overcome by the addition of bromide ion (5.0×10^{-4} mol dm^{-3}) as a masking agent. The interference from iodide, thiosulfate, sulfide, and cyanide ions could be overcome by a preliminary treatment with silver(I), and that from sulfite and nitrite ions with permanganate and hydrogen peroxide. The results are shown in Table 2.

Composition of the Ternary Complex Formed. The palladium(II)-to-thiamine ratio and (palladium/thiamine)-to-Phloxine ratio determined by Job's method of continuous variation were 1 : 2 and 1 : 1, respectively. The ternary complex formed may be expressed as $\{\mathrm{Pd^{II}(thiamine)_2}\}\mathrm{(Phloxine)}$.[7]

Application. The proposed method was applied to the assay of palladium in palladium carbon and palladium asbestos. The palladium in the samples was readily dissolved in aqua regia, the insoluble residue being removed by filtration. The obtained results were in good agreement with those obtained by the KI method, the MTK method and ICP-AES. The recoveries of palladium(II) from each sample were about 98—103%. The results are given in Table 3.

Study for Membrane Filter Preconcentration Technique. A membrane filter preconcentration technique was investigated for the purpose of enhancing the determination sensitivity. Only the use of a surfactant was examined to improve the sensitivity and reproducibility under the same conditions for the standard procedure for spectrophotometry. Only PEG was effective among the various surfactants tested. Several filters of different sorts and pore sizes were examined to collect the ternary-complex aggregates. A nitrocellulose membrane filter was suitable since it readily dissolves in organic solvents. Constant absorbances were obtained over a range of pore size, from 0.2 to 0.65 μm; the absorbances decreased with increasing pore size of the membrane filter. A 0.65 μm pore size was subsequently used because of the higher filtration rate. Of the organic solvents examined, DMSO was the best with respect to the high absorbance and low deviation. The absorption spectra of Solutions A′ and B′ are shown in Fig. 2.

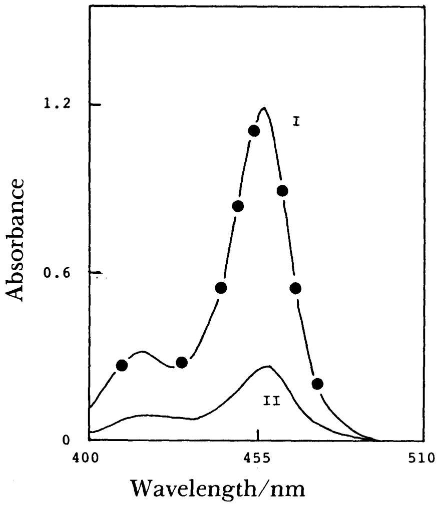

Fig. 2. Absorption spectra of Phloxine-thiamine-palladium(II) DMSO solution (Solution A′) and Phloxine-thiamine DMSO solution (Solution B′) after membrane filter preconcentration technique. Pd(II): 0.42 μg; Reference: DMSO.
Curve I(—●—), Solution A′; Curve II(——), Solution B′.

Table 3. Determination of Palladium Carbon (Pd-C) and Palladium Asbestos (Pd-A)

Sample	Pd, Amount/%				Recovery test[a] of proposed method	
	Proposed method	KI method	MTK method	ICP-AES	Recovery[b] /%	R.S.D.[c] /%
5% Pd-C	4.75	4.73	4.76	4.70	101.6	1.00
10% Pd-A	9.60	9.71	9.60	9.80	100.1	0.73
20% Pd-A	19.40	19.31	19.32	19.40	102.8	0.70
30% Pd-A	30.54	30.58	30.32	31.00	98.8	0.86

a) Mean of 5 determinations. b) Palladium taken, 2.1 μg/10 ml. c) Relative Standard Deviation.

This procedure is more than 20 times as sensitive as the method employing aqueous medium. Analytical values of 5% palladium carbon and 20% palladium asbestos in Table 3 were 4.60% and 19.20%, respectively.

Furthermore, since Solutions A′ and B′ emitted fluorescence, fluorimetry could be used. The difference in the relative fluorescence intensity between Solutions A′ and B′ at 575 nm of emission wavelength with excitation at 520 nm was measured.

In general, the formation of a ternary-complex results in a quenching of the fluorescence[3] of the dye used. Nevertheless, the fluorescence intensity of Solution A′ was larger than that of Solution B′. The absorption spectrum and the emission spectrum of an independently prepared Phloxine DMSO solution were almost identical to that of Solutions A′ and B′. It is probable that the ternary-complex aggregate collected on a membrane filter dissociates to form at least two components, $\{Pd^{II}(\text{thiamine})_2\}$ and Phloxine. The latter will give a fluorescence and absorption spectrum in a DMSO solution. The reason why the method with a membrane filter preconcentration technique gives an abnormally highly sensitivity ($\varepsilon > 10^6$) is probably that a few Phloxine molecules associate with the ternary complex and a bulky aggregate forms.

The surface of membrane filters was observed with SEM. In the case of depth-type (networks) membrane filters, a little difference was recognized between the sample (photograph(c)) and the reagent blank (photograph(d)), whereas a large difference was observed between the sample (photograph(a)) and the

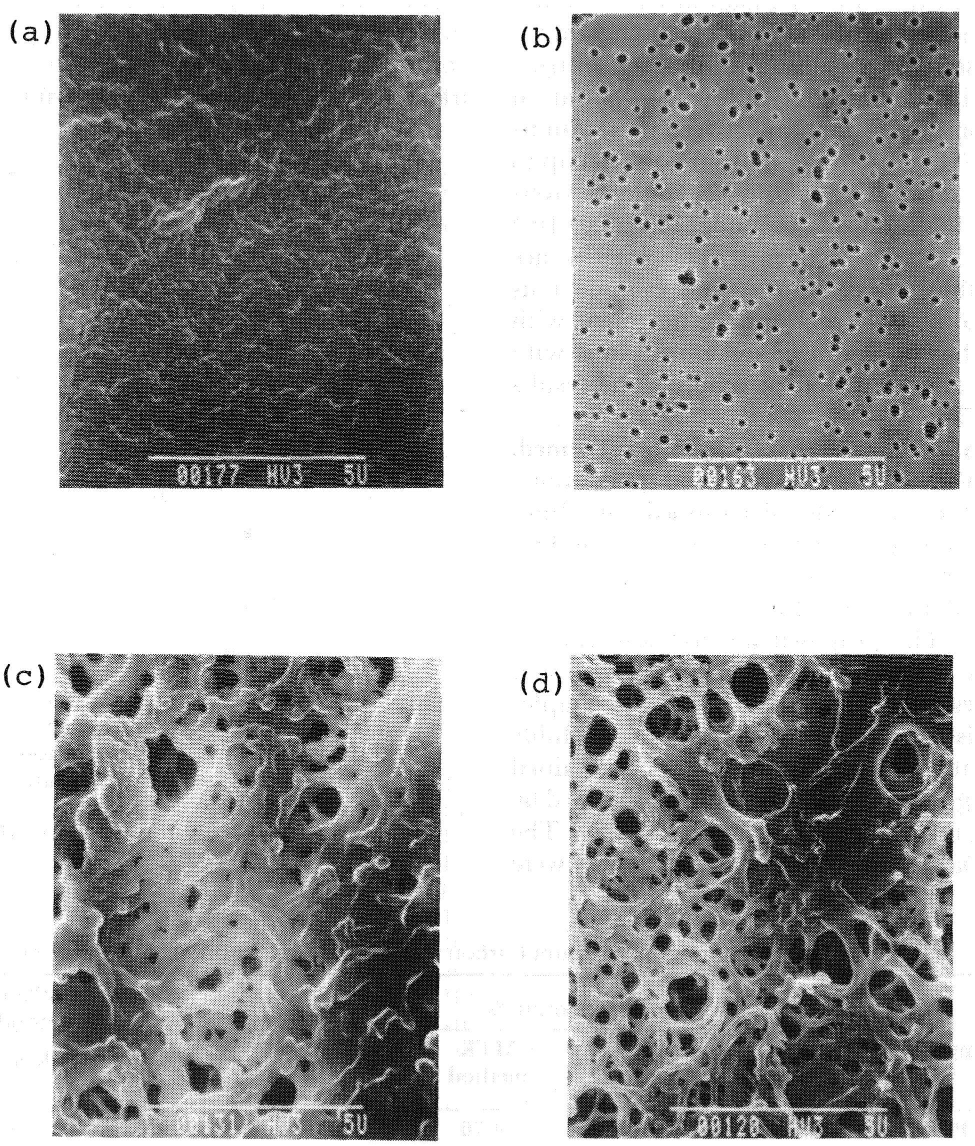

Fig. 3. Scanning electron microscope (SEM) pictures of the aggregates collected on membrane filters.
(a) Sample (Phloxine-thiamine-palladium(II)) on screen-type filter. (b) Reagent blank (Phloxine-thiamine) on screen-type filter. (c) Sample on depth-type filter. (d) Reagent blank on depth-type filter.

reagent blank (photograph(b)) in screen-type (holes) membrane filters. Thus, the collection of aggregate on membrane filters was found to depend not on the adsorptivity but on the molecular size. These photographs are shown in Fig. 3. This point should be studied in greater details.

Conclusion

A simple, sensitive and selective spectrophotometric method of palladium(II) with Phloxine as {**R**} and thiamine as {**L**} was established. The method was applied to the assay of palladium in practical samples, and the analytical results were in good agreement with those obtained by other methods. The sensitivity was enhanced by about 20 times over spectrophotometry and/or fluorimetry (probably by measuring free Phloxine in DMSO) by combining a membrane filter preconcentration technique. It was suggested by observing with SEM that the collection of aggregate on a membrane filter should depend on the molecular size. Though further investigations are necessary for the application of this method to a variety of samples, including the development of the membrane filter preconcentration technique, the proposed method should be useful and convenient for a simple, sensitive determination of palladium(II).

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1) This paper is Part LXXXI of a series entitled "Application of Xanthene Derivatives for Analytical Chemistry". This work was presented at 108th Annual Meetings of Pharmaceutical Society of Japan in Hiroshima, April 1988.

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