

SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF PALLADIUM: A REVIEW

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REVIEW

The work done on spectrophotometric determination of palladium (since 1976) has been reviewed and is presented in tabular form in the subsequent pages. The available information has been condensed and is presented under different columns; name of the reagent, λ max or working wave length with ϵ , pH, remarks and references. Under the column remarks the procedure, composition of the complex, sensitivity, interference studies etc. have been described in condensed form.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Mepazine (pecazine) hydrochloride	515 nm	2.65	Palladium (II) forms a pink 1:1 complex with the reagent at pH 2.65 (HCl-Na acetate buffer), and its absorbance is measured against a reagent blank. Beer's law is obeyed for up to 12 ppm of Pd. Interference is caused by EDTA, $S_2O_3^{2-}$, Ag and Au (III) and by > 1.6 ppm of Ru (III), 2 ppm of Fe(II) or Pt(IV), 5 ppm of I ⁻ , 6 ppm of Ir(III), 12 ppm of Rh(III) and 20 ppm of Os(VIII).	1
Eriochrome cyanine R (C.I. Mordant Blue 3)	630 nm	4.5	Determination of rhodium and palladium in platinum alloys with the reagent is reported. For Pd, the sample is decomposed with aqua regia, the solution is evaporated and the residue is dissolved in HCl. Pd is absorbed on Amberlite IRC-50 resin (Na ⁺ form) from 0.1M-HCl medium. The Pd is eluted from the Amberlite with 50 ml of 1M-HCl. A portion of eluate is diluted to 10 ml, and to a 1-ml aliquot are added 2.5 ml of mM-Eriochrome cyanine R, 0.5 ml of 10 mM cetylpyridinium bromide and 2.5 ml 0.2M-acetate buffer of pH 4.5. The mixture	2

is heated for 20 min. at 50° on a water bath then diluted to 25 ml. and the absorbance is measured against a reagent blank. For Pt and Rh, 0.2M-acetate buffer of pH 3.4 is used and the absorbance is measured at 630 nm against a reagent blank.

**Benzothiazole-2-aldehyde
-2-quinolyl hydrazone in
presence of Cl⁻**

647 nm **≈1M**
 H₂SO₄

A 1:1:1 complex of Pd(II) is formed in H₂SO₄. A medium with the reagent and Cl⁻. An aliquot of sample solution 3M-H₂SO₄ (3.5 ml) and 0.02M-NaCl (1.5 ml) are mixed and the solution is diluted to 10 ml with H₂O and equilibrated with 0.25M-reagent in benzene (10 ml) for ≈10 minutes and then the absorbance of the ternary complex in the extract is measured against a reagent blank. Due to high selectivity of the reagent, Pd can be determined in the presence of many other ions, but Ag, I⁻, SCN⁻ and EDTA must be absent.

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Glyoxal bis-(thiosemicarbazone)	600 nm $\epsilon=2500$	1.0-9.5	The reagent forms a stable 1:1 (Pd:R) complex in aq. 50% dimethylformamide medium. In the presence of EDTA as masking agent, only Pd(II) forms a stable (blue) complex, thus permitting selective determination of 0 to 51 μg of Pd in 25 ml of final solution at pH 2 to 4 (adjusted with acetic acid). The Sandell sensitivity index is 0.042 $\mu\text{g}/\text{cm}^2$. Up to 500 μg of Ag and Hg(II) and 1000 μg each of Pt(II), Fe(II), Fe(III), Co, Ni, Cu(II), Pb, Sn(II), Sn(IV), Ga(III) and Mo(IV) can be tolerated. This reagent also forms a 1:1 complex with Ni at pH 3.5 to 11, with Cu(II) at pH 3 to 10 and with Zn and Cd at pH 9 to 11.	4

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-(Mercaptoacetamido)pyridine [N-(2-pyridyl)-2-mercaptoacetamide]	440 nm	2.8-8.6	This reagent reacts with Pd(II) to form a 1:2 (PdR) complex that is stable for 24 hours. Beer's law is obeyed for 0 to 15 ppm of Pd(II), and the sensitivity of the reaction is 2.4 ng/ml. In the determination of 1.22 ppm of Pd(II) at pH 6.6, there is no interference from 340 ppm of Zn or Mn(II), 180 ppm of alkali or alkaline earth metals, 100 ppm of Cr(II) or Ir(III), and 60 ppm of Sb(III), Pb(II) or Sn(II). Divalent Co, Rh(II), Pt(IV) and Ru(III) react with the reagent in a similar manner to Pd(II) and must therefore be absent. Fluoride and tartrate must also be absent.	5
Thiobenzoyl acetone (3-mercapto-1-phenyl-but-2-en-1-one)	450 nm $\epsilon=9930$	3.8-6.6 (pH 5 preferred)	Palladium (2 to 100 μ g) is extracted quantitatively from 25 ml of aq. solution buffered at pH 3.8 to 6.6 by shaking for 20 min. with 10 ml of 1 mM reagent in benzene and the absorbance is measured. It is reported that Ru(III) interferes strongly but Rh(II), Os(III), Ir(III) and Pt(IV) do not interfere up to at least a 40-fold excess.	6

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Ref.
1-(2-Quinolylazo) acenaphthylene 2-ol	670 nm $\epsilon=14200$	2.2-3.0	Palladium(II) forms a 1:1 (Pd:R) green complex with this reagent at pH 2.2 to 3.0 in a medium of 5% methanol. The complex is extracted into CHCl ₃ for spectrophotometry. The optimum range of the method is 3.5 to 7.4 ppm of Pd. Sandell's sensitivity index is 7.5 ng/cm ² . Beer's law is obeyed for 3.2 to 11.6 ppm of Pd. The ions I ⁻ , S ₂ O ₃ ²⁻ , CNS ⁻ , CN ⁻ , thiourea and EDTA interfere seriously. In the determination of 4.24 µg/ml of Pd the tolerance limits of diverse ions which did not cause deviation of more than $\pm 2\%$ in absorbance are: NO ₂ ⁻ , NO ₃ ⁻ , Ac ⁻ , BO ₃ ³⁻ , PO ₄ ³⁻ (400); oxalate, citrate tartrate, SO ₄ ²⁻ (100); F ⁻ , Br ⁻ (50); Zn(II), Cd(II), Co(II), Ni(II), V(V), Pb(II), Ba(II), Sr(II), UO ₂ (II), Ti(II), Cr(II) (1000); Hg(II), Fe(II) and Fe(III), Mn(II), In(III) (250); Ag(I), Au(III), Tl(IV), Pt(IV) (100); Cu(II) (20); Ru(III), Rh(III), Ir(III) (5); Os(VIII) (2)	7

550 nm 8.0-10.6 Pd(II) also forms a 1:2 (Pd:R) red complex with this reagent at pH 8.0 to 10.6. The complex can be extracted into CHCl_3 for measurement of absorbance. The optimum range is 1.1 to 5.0 ppm of Pd and the Sandell sensitivity is 4.9 ng/cm^2 . Beer's law is obeyed for 0 to 7.15 ppm of Pd. The ions CN^- , I^- , NO_2^- , CNS^- , thiourea, $\text{S}_2\text{O}_3^{2-}$ and F^- interfere seriously. In the determination of 3.39 $\mu\text{g/ml}$ of Pd, tolerance limits of diverse ions are: Br^- , NO_2^- , tartrate (1000); PO_4^{3-} (500); Co(II) , Ni(II) , Cu(II) , Hg(II) (25) (masked with EDTA), citrate (200); EDTA (150); Zn(II) , Cd(II) (40) (masked with EDTA); Ti(II) , V(V) , W(VI) , Mo(VI) , Ag(I) , Sn(II) , Ba(II) , $\text{UO}_2(\text{II})$, Ge(IV) , Al(III) (20); Au(I(II)) (10); Os(VIII) , Ru(III) (5).

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thiotropolone	520 nm $\epsilon=5900$	3.0-7.5	This reagent forms a 1:2 red complex with Pd(II) at room temperature. For measurement at 520 nm the optimum analytical ranges are 2.63 to 13.0 ppm for Pd. The Pd complex is formed in media of pH 3.0-7.5 and extracted into CHCl_3 and absorbance is measured. Beer's law is obeyed for 0.0 to 13.8 ppm of Pd. The Sandell sensitivity index is 18 ng/cm ² for Pd. Sulphite, thiosulphate, oxalate, EDTA and CN ⁻ interfere seriously. The tolerance limits of diverse ions in ppm are: Rh(III), Zn(II) (15); Ru(III), Ga(III), Sb(III), Cd(II) (20); In(III) (25); Mn(II), Pt(IV) (30); Os(VIII) (40); Ir(IV), Sn(IV), Mo(VI) (50); Pb(II) (100); Iodide(200); Sr(II), Mg(II) (500); nitrite (600); tartrate, citrate, thiourea, thiocyanate, phosphate, bromide (1000); F ⁻ , SO_4^{2-} (2000) and NO_3^- (5000);	8

Hg(II) (50) (masked with 500 ppm I⁻); V(IV) (50) (masked with 100 ppm F⁻). The reagent has also been used for determination of Rh(III) and Os(VII). On heating Rh(III) forms a 1:3 brown complex and Os(VIII) forms a 1:1 brownish red complex. The Rh(III) complex is extracted at pH 7.5 into CHCl₃ and absorbance is measured at 500 nm where its absorbance of the Os(VII) complex at pH 4.5 is measured in 5% acetone at 540 nm. The optimum analytical ranges (ppm) are 0.79 to 3.55 for Rh and 0.65 to 4.1 for Os. Beer's law is obeyed for 0.0 to 4.1 ppm of Rh(III) and 0.0 to 4.6 ppm of Os(VII). Sandell's sensitivity index (mg/cm²) is 4 for Rh and 15 for Os.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1,3-Diphenylthiourea (DPT)	340 nm	2N to 6N HCl	A measured amount of Pd(III) solution is introduced into a 100 ml separatory funnel diluted with water and its acidity is maintained at 2N to 6N. To this 1 to 2 ml of 0.01M-DPT solution is added, stirred and allowed to stand for 5 minutes and mixed with 2-3 ml of ethanol. The yellow palladium-DPT complex formed is extracted three to four times with 3 ml portions of CHCl ₃ . The combined extract is diluted to 25 ml with CHCl ₃ and its absorbance is measured against the reagent blank. Beer's law is obeyed for 0.47 to 5.92 $\mu\text{g/ml}$. However, Pt(IV), Rh(III), Ir(III), Os(VI) and Ru(III) have also been determined with the same reagent. The λ_{max} (nm), optimum pH or acidity range for the individual complexes are: 320 (0.25-5.0 N HCl) and 310 (pH 4.4 to 5.6) with Pt(IV); 315 (at 3.5 to 5.0 N HCl) and 300 (at pH 3.0 to 5.5) with Rh(III); 310 (at pH 5.25 to 6.20) for Ir(III); 315 and 510 (0.1N to 2.5N HCl acid) with Os(VI); 305 and 510 (at 3.0 to 4.5 N HCl) and 340 (pH 4.20 to 5.65) with Ru(III).	9

Analysis of palladium - nickel - copper alloys by using the reagent is discussed. This reagent forms a complex with Pd(II) in a medium 0.1M to 5.0M in H₂SO₄ and the absorbance is measured. Beer's law is obeyed for 0.5 to 5 µg/ml of Pd; two-fold amounts of Ni and Cu relative to Pd do not interfere. A method based on these facts has been used for determining 20 to 40% each of Pd, Ni and Cu in alloys. However, complexes of Ni(II) and Cu(II) with the reagent are formed at pH 4.3 and 1.1 to 1.3 and have λ_{max} at 525 nm (ε=52,000) and 535 nm (ε=11,800) respectively. Beer's law is obeyed for 0.1 to 0.9 µg/ml of Ni and 0.5 to 3 µg/ml of Cu.

580 nm
ε=11700
1.0-5.0M
H₂SO₄

4-(2-Pyridylazo)
resorcinol

All three reagents have been used for determination of Pd(II). Beer's law is obeyed over the ranges 0.2 to 11.3, 0.32 to 10.6 and 0.12 to 10.6 ppm for reagents I, II and III respectively. Silver, Hg(II), Os(III) and Ru(III) interfere but Pt(IV), Rh(III), Fe(III), Fe(II), Cu(II), Ni(II) and Co(II) do not interfere.

550 nm
550 nm
520 nm
1.0-10.0
1.0-7.5
1.0-8.0

Derivatives of 5-sulpho
benzoic acid
2-(6-Hydroxy-m-tolyl azo) (I)
2-(5-Chloro-2-hydroxy
phenylazo) (II)
2-(2-Hydroxy-5-sulpho
phenylazo) (III)

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1.10-Phenanthroline and eosin	540 nm	6.0-8.0	Palladium(II) forms a 1:2:1 (Pd:1.10-phenanthroline:eosin) complex in aq. medium of pH 6 to 8 (10 ml) containing 0.01% of 1.10-phenanthroline and 0.01% of eosin. The complex is extracted into CHCl_3 (6 ml) and absorbance is measured. Beer's law is obeyed for 0.02 to 0.5 $\mu\text{g/ml}$ of Pd. The reagent is less selective than α -furyldioxime. Lead, Cu, Ni, Co, Pt and Os do not interfere, but Ag, Ru and Fe(II) do.	12
1-(2-Pyridylazo)ph :naphthrene 2:0:1	665 nm	3.0-7.0	A methanolic solution of the reagent forms a complex with Palladium(II) in acetate-buffered medium of pH 3.0-7.0. The complex is extracted into CHCl_3 and absorbance is measured. The Sandell sensitivity is 13 ng/cm^2 , and the analytical range is 2 to 12 ppm. The reagent has also been used for the determination of Ru and Rh in acetate buffered medium of pH 4.7 to 6.1 and 4.0 to 8.0 at 615 and 625 nm respectively. The Sandell sensitivities (ng/cm^2) are 4.9 for Ru and 4.8 for Rh.	13

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1-(4-Bromophenylazo)-2-naphthol (I)	510 nm $\epsilon = 12900$	0.75M H_2SO_4	These reagents (I and II, respectively), form 2:1 complexes with Pd(II) in a medium made 0.75M in H_2SO_4 , 0.45 in Cl^- and 2.3 mM in I or II. The complexes are extracted into benzyl alcohol and show maximum absorbance at 510 nm and 500 nm respectively. In the case of Pd(II)-I complex, Beer's law is obeyed for 1 to 5 $\mu g/ml$ of Pd (at the optimum wave length of 570 nm). In the case of Pd(II)-II complex, Beer's law is obeyed for 1.5 to 5 $\mu g/ml$ of Pd (at 570 nm).	14
1-(3-Chlorophenylazo)-2-naphthol (II)	500 nm $\epsilon = 12500$	0.75M H_2SO_4		
6-Methyl picolinaldehyde azine	405 nm	5.7-8.25 or 4.7	To the solution containing Pd(II) chloride (115 to $\approx 1000 \mu g$) add 10 ml of a 0.2% solution of the reagent in ethanol, and then either the pH is adjusted to 5.7 to 8.25 or 10 ml of an acetic acid Na-acetate buffer solution of pH 4.7 is added. The solution is diluted to 50 ml with H_2O , and the absorbance is measured. Rh(III), Ru(IV) or Pt(IV) ions interfere at a concentration equal to that of Pd(II), and Os(VIII) at higher concentration.	15

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Mercapto-propionanilide	405 nm	0.1-2N H_2SO_4	The sample solution (0.1 to 15 $\mu g/ml$ of Pd) 0.2 to 2N in H_2SO_4 is prepared, and 2 ml of fresh 5% solution (in ethanol or methanol) of 2-mercapto-propionanilide is added and then diluted to 20 ml. After 10 min the complex is extracted into $CHCl_3$ (10 ml), and after a further 15 min, the absorbance of the extract is measured. There is no interference from 1000-fold amounts of Pt(IV), Rh(III), Os(IV), Ru(IV), Fe(III), Co(III), Ni(II), Cr(III) or Al; up to 200-fold amounts of Bi(III), Zn, Pb(II) or MoO_4^{2-} can be masked by adding 2 g of tartaric acid to the solution.	16
6-Methyl-picolinaldehyde-2-quinolyl hydrate	400 nm	5.3	The test solution, containing 2 to 12 ppm of Pd, is treated with 5 ml of a 4 mM solution of the reagent in aq. 50% ethanol and with a buffer solution of pH 7.3. The solution is diluted to 25 ml and the absorbance is measured, in the determination of 10 ppm of Pd, no interference is caused by up to 20	17

				ppm of Fe, Cr(II), Al, Zr, Ru(III), Th, In(III), W(VI) or Be or by up to 40 ppm of Ag, Pb(II) C-1, Co, Zn, Mn(II), La, Y, U(VI), Mg, Ca, Sr or Ba.	
Pyridoin phenylhydrazone	450 nm	4.75		The reagent forms a 1:2 (Pd(II):R) complex with the Pd. The test solution containing 25 to 100 µg of Pd is treated with 0.5M-KNO ₃ (2 ml), acetate buffer solution of pH 4.75 (5 ml) and ethanolic 0.1% reagent (10 ml); diluted to 25 ml with H ₂ O, and after 30 min, absorbance is measured. Other platinumoids in large excess interfere and S ₂ O ₃ ²⁻ weakens the colour. EDTA has been used to mask interference from Cu and Ni.	18
D(-2-pyridyl) ketone azine	405 nm 420 nm 405 nm	2.0 2.0 4.7		The reagent forms a yellow 1:1 complex with Pd(II). The absorbance of the solution is measured at pH 2.0 (405 nm) for 3.9 to 8.0 ppm of Pd or at pH 2.0 (420 nm) for 2.8 to 10 ppm or at pH 4.7 (405 nm) for 2.3 to 9.2 ppm of Pd. Errors are ±0.33%.	19

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(4,5-Dimethyl-2-thiazolylazo)-2-methylresorcinol	560 nm	Tris-HCl buffer	To the test solution, containing 0.08 to 0.76 ppm of Pd(II), are added 10 ml of a methanolic 0.1 mM solution of the reagent, 2.5 ml of 1.0M-KCl and 2.5 ml of Tris-HCl buffer solution. The solution is diluted to 25 ml with H ₂ O and the absorbance is measured against a reagent blank. The relative error is $\pm 0.73\%$ in the range 0.25 to 0.76 ppm of Pd(II). Most interfering species present in concentration not exceeding that of Pd(II) can be masked with F ⁻ or 1,2-diaminocyclohexanetetracetic acid.	20
5,10,15,20-Tetraphenylporphine trisulphonate	434 nm $\epsilon=500000$ 411.6 nm $\epsilon=280000$	2.5 2.5	The formation of the complex between Pd and the reagent is accelerated by 20 μ M to 0.2 mM L-ascorbic acid. The complex is formed (pH 2.8 to 7.0) within 7 min. at 100° and is stable at pH 2 to 11 for 12 hours. To 15 ml of sample solution (containing 1 to 6 μ g of Pd(II)), 6 ml of 10 μ M reagent, 1 ml of 1 mM L-ascorbic acid and 1 ml of 1M acetic acid (pH 3) is added. The mixture is	21

heated in a boiling water bath for 8 min. and then allowed to cool. To it 1 ml of 1M chloroacetic acid is added, diluted to 25 ml with water (pH 2.5) and the absorbance of the solution is measured against a reagent blank at either of the wave lengths of maximum absorbance. There is no interference from 500 μg of Ba, Cd, Ni(II), Pb(II) or VO_3^- ; 50 μg of Al, Ca, Co(III), Cr(III), Ga, Mg, Mn(II), Mo(VI), VO(II), W(VI) or Zn, or 5 μg of Ag(I), Fe, In, Pt(II) or Sn(II); whereas 5 μg of Cu(II), or Hg(II) interfere. At 411.6, Beer's law is obeyed for up to 250 ng/ml of Pd(II) and the sensitivity (0.001 absorbance unit) is 0.494 ng/cm².

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thioantipyrine	230 nm $\epsilon \approx 36500$	3.5 or 10.0	Palladium(II) forms three complexes with the reagent. The 1:4 complex formed in the presence of excess of reagent is the most suitable for determining μg amounts of Pd. The test solution (containing $< 75 \mu\text{g}$ of Pd) is mixed with acetate (pH 3.5) or borate (pH 10) buffer solution (2 ml) and 0.2% reagent solution (2 ml), the mixture is diluted to 25 ml with H_2O , and the absorbance is measured against a reagent blank. The calibration graph is rectilinear for up to 3 $\mu\text{g}/\text{ml}$ of Pd. Fe(III), Hg(II) and V(V) should be absent; permissible upper limits for Cu, Ce(IV), Ag, Au(III), Ru(III) and Pt(IV) range from ≈ 100 to $\approx 500 \mu\text{g}$.	22
α -Furildioxime	380 nm $\epsilon=21000$	4.5	The aq. test solution (40 ml; 5 to 50 μg) is placed in a stoppered 100 ml conical flask and to it ethanolic 0.1% reagent (2 ml) is added; the pH is adjusted to 4.5 with ammonium acetate buffer solution. It is mixed thoroughly and the Pd chelate is	23

allowed to separate. To it 20% naphthalene solution in acetone (2 ml) is added, the mixture is shaken vigorously for 1 min. and filtered. The residue is washed with water and dried in an oven at 50° to 60°. The dried material is dissolved in CHCl₃ and the absorbance of the solution is measured against a reagent blank solution. Palladium 5 ng/ml gives an absorbance of 0.001. The level coefficient of variation at 25 µg level is 0.8%. Iron(III), Bi(III), Au(III) and CN⁻ interfere seriously.		5-Diethylamino-2-nitrosophenol	540 nm ε=23300	Acidic	The reagent reacts with Pd to form a red 1:2 (Pd:R) complex that is stable in acidic aq. solution. The method has been used to determine Pd in catalysts for purifying car-exhaust gases.	24
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Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Reis.
Dithiopyrylmethane[4,4'-methylene: bis-(1,5-dimethyl-2-phenyl)pyrazoline-3-thione]	500 nm	6M H_2SO_4	The reagent has been used for determination of Pd in iron based alloys. The sample (0.1 to 0.5 g) is dissolved in HCl (1:1) and 1 to 2 ml of HNO_3 ($d=1.19$) is added and boiled for 20 min. to decompose the carbides, then 8 to 10 ml of conc. H_2SO_4 is added, evaporated to fumes and the residue is dissolved in 6M- H_2SO_4 . To an aliquot of this solution 3 to 8 ml of 10% tartaric acid solution and 1.3 to 3.0 ml of a solution of the reagent (1 mg/ml) in 6M- H_2SO_4 are added and diluted to 50 ml with 6M H_2SO_4 and the absorbance is measured. The Pd conc. is determined from a calibration graph. The sensitivity of the method is 1.6 ppm. Large amounts of Co, Cr, In, Ti, Bi, Sb, Zr, Sc, rare-earth elements, Mo, Ni, Tl, Be, V(V), Mn and Al can be tolerated; Fe(III) which forms an intensely coloured complex with the reagent is masked by the ascorbic acid.	25

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Nitroso-N-phenyl dibenzyl amine	522 nm	Mineral acids	The complex formation (red complex) occurs between Pd, an anion and four molecules of the reagent, which is stable in mineral acids and is extracted into CHCl_3 -ethyl acetate (3:1) for measurement of absorbance. Beer's law is obeyed for 0.005 to 1 $\mu\text{g/ml}$ of Pd. Common acids e.g. HClO_4 and HCl interfere and the presence of Cl^- is undesirable except in low concentration. The variance is 67% for plant ash containing < 0.12 μg of Pd, 53% for soil samples containing 0.01 to 0.06 μg of Pd.	28
2-Pyridyl-2-thienyl- β -ketoxime	433 nm	0.0-7.0	The complex between Pd(III) and the reagent is stable in the pH range 0 to 7. The complex is formed at 45° , and is extracted into CHCl_3 and absorbance is measured. Beer's law is obeyed for 0.15 to 2.1 ppm of Pd(III). At pH 4.5, and in the presence of EDTA, up to 100 mg of Cu does not interfere in the determination of 26 μg of Pd. Platinum, Rh(III), Ir and ClO_4^- interfere seriously.	29

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref.
Nitroxaminazo [4-amino-3-(2-hydroxy-5-nitro-3-sulphophenylazo) naphthalen-2,7-disulphonic acid]	470 nm	0.5 M H_2SO_4	Palladium is determined in ores and products of pyrometallurgy. The sample (0.5 to 1.0 g) is dissolved by heating it with 30 ml of aqua regia and 1 to 2 ml of bromine is added to remove free S, and NH_4F and HF to remove SiO_2 . The solution is evaporated and the moist residue is dissolved in 10 ml of conc. HCl and evaporated to remove HNO_3 . The residue is dissolved in 15 ml of 1M- HCl , and a suitable aliquot is added to 200 ml of HCl and 300 mg of modified Milton-T fibre and boiled for 30 min. A medium porosity filter is used to separate the fibre, together with the Pd and other Pt group metals. The material on the filter is washed with hot HCl and filter and contents are transferred to a porcelain crucible, ignited at 700° to 800° ; the residue is dissolved in 5 ml of H_2SO_4 (1:1), heated to fumes, and 5 to 7 drops of 30% H_2O_2 solution are added. After evaporation to dryness, the residue is dissolved in 5 ml of	26

1M-HCl, boiled, cooled and 5 ml of H ₂ O, 2 ml of 5M-H ₂ SO ₄ , 1 ml of 10% hydroxyl-ammonium chloride solution and 2 ml of 85% H ₃ PO ₄ are added. After 210 min. 2 ml of 0.1% reagent solutin is added, heated at 90° for 30 min, cooled, diluted to 20 ml with H ₂ O and the absorbance is measured. The sensitivity is 2 ppm of Pd in the sample.				27
Phenyl methyl phosphon-amidothionate	440 nm	Acidic (HBr)	0.5 ml of test solution are mixed with about 4.25 ml of 2M-HBr. This is boiled for 5 min., cooled and 0.25 ml of 1M-SnBr ₂ in 2M-HBr is added and set aside for 20 min. It is extracted with 5 ml of a 0.1M solution of the reagent in CHCl ₃ , and the absorbance of the extract is measured against CHCl ₃ . Beer's law is obeyed for 1 to 200 µg of Pd. Other Pt group metals, Cu, Fe, Ni, Co, SO ₄ ²⁻ and Cl ⁻ do not interfere.	

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
α -(Phenylazo) benzal-doxime	550 nm	≈ 2	An ethanolic solution of the reagent reacts with Pd(II) in a 1:ethanol of pH ≈ 2 to form a complex suitable for direct spectrophotometry. The optimum analytical range of the method is 2 to 16 ppm of Pd. Cyanide interferes (but up to 1 mg can be masked by adding Zn); Au(III), Ag, Pt(II), Ru(II), Rh(III), Os(VIII) and Ir(III) in amounts 20 times that of Pd and I ⁻ and Br ⁻ in amounts 5 times that of Pd, do not interfere.	30
Eriochrome cyanine R (C.I. Mordant blue 3) and cetyltrimethyl ammonium ions	600 nm $\epsilon=93000$	5.5-6.0	To determine Pd, the absorbance of the Pd-Eriochrome cyanine R - cetyltrimethyl ammonium 1:2:3 complex in a Na-acetate buffer of pH 5.5 to 6.0 is measured. Cu(II), Be, Al, Ga, In, Sc, Fe(III), EDTA, tartrate and citrate interfere strongly	31

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Furoin thiosemicarbazone	360 nm $\epsilon=19800$	6.0	To the test solution containing up to 75 μg of the metal is added a 2 ml portion of 0.1% reagent solution in methanol. The pH is adjusted to 6.0 with dil. HCl or NH_3 , the solution is diluted to 25 ml and the absorbance is measured against a reagent blank. The apparent instability constant is 3×10^{-12} for the Pd complex. This method has been used to analyse Pd in palladised charcoal samples. This reagent has also been used for determining nickel(II) and copper(II). The pH is adjusted with dil. HCl or NH_3 to 9.0 for Ni(II) and 3.0 for Cu(II). The absorbance against a reagent blank is measured at 360 nm for Ni(II) and 355 nm for Cu(II). The Ni complex is also extracted into CHCl_3 and measured at 410 nm. The respective ϵ values and apparent instability constants are 1.54×10^4 and 6.5×10^{-11} for the Ni complex and 1.45×10^4 and 7.1×10^{-7} for the Cu complex.	32

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5,10,15,20-Tetrakis-(4-sulphophenyl)porphine	410 nm $\epsilon=220000$	≈ 3.6	Determination of micro amounts of Pd is done by using the Soret-band of the complex of Pd(II) with this H ₂ O-soluble porphyrin. Complex formation in aq. medium is slow at room temp., but proceeds quantitatively at pH ≈ 3.6 , and a stable 1:1 complex is formed when the reaction mixture is heated at $\approx 100^\circ$ for 15 min. The Soret-band of the complex at 410 nm, is well separated from that of the diacid form of the reagent (at 435 nm). the calibration graph is rectilinear for up to at least 360 ppb of Pd. Sensitivity is 0.48 ng/cm ² .	33
α -Furildioxime	380 nm	Acidic	Determination of traces of gold, palladium and platinum in presence of large amounts of copper and nickel is reported. The sample containing 11 to 19% of Cu and 8 to 89% of Ni is dissolved in aqua regia, the solution is evaporated, the residue is dissolved in 1M-HCl, and Au is extracted with amyl acetate and determined with	34

Brilliant green and the absorbance is measured at 630 nm. For determination of Pd, the aq. phase is mixed with the reagent, the complex formed with Pd is extracted into CHCl_3 , and absorbance is measured. Platinum is determined at 405 nm in the remainder of the aq. phase extracted with 5% triethylamine solution in CHCl_3 . Down to 1 ppm of Pd could be determined.

Tetramethylthiuram
[bis-(dimethylthiocarbamoyl)] disulphide

310 nm

2.5-3.5

35

Palladium(II) is extracted from aq. solution at pH 2.5 to 3.5 into an $\approx 0.09\text{ mM}$ solution of the reagent in toluene (or benzene) to form a yellowish complex. Beer's law is obeyed for 0.2 to 1.4 $\mu\text{g/ml}$ of Pd. Determination of Pd is possible in the presence of other Pt group metals except Os, Iron(III), Ni(II), Ga, In and Tl (can be masked with EDTA and WO_4^{2-} and V with tartaric acid and NH_4F respectively).

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref's.
Derivatives of 1,4-dihydro-4,4,6-trimethylpyrimidine-2-thiol The complexes of Pd(II) with substituted pyrimidinethiols and 2-amino-4,6-dimercapto-1,3,5-triazene are studied. The absorption max., optimum pH of acidity range and ϵ values for individual complexes are shown in the table. Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$) is 0.025, 0.020, 0.019 and 0.026 (at 318 nm) for complexes with I, II, III and IV (at 400 and 318 nm) respectively. Beer's law is obeyed over the ranges 5.6 to 16.0; 4.3 to 19.0 3.2 to 12.8 and 5.0 to 12.0 ppm of Pd(II) for the complexes with I, II, III and IV respectively. The complex of I is fully extractable and that of II partially extractable into CCl_4 or CHCl_3; the III and IV complexes are not extractable. Thiourea, CN^-, SCN^-, I^-, $\text{S}_2\text{O}_3^{2-}$ and Au(III) interfere in all instances				
1-Propyl (I)	430 nm ($\epsilon=4200$)	0.2-10N HCl		
1-(2-Amino-p-tolyl) (II)	440 nm	0.2-0.6N		
1-(5-Amino-6-hydroxy-2-mercaptopyrimidin-4-yl) (III)	380 nm ($\epsilon=5600$)	3-4N HCl		
2-Amino-4,6-dimercapto-1,3,5-triazene (IV)	318 nm ($\epsilon=15200$) 400 nm ($\epsilon=4000$)	10-11.5		

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Sodium ethyltrithio-carbonate	370 nm ($\epsilon=12770$) 448 nm	1.0-10.0	Palladium(II) forms a 1:2 complex with the reagent, which can be extracted quantitatively into CCl_4 at pH 1 to 10. The complex has λ max at 370 nm and 448 nm. At 370 nm, Beer's law is obeyed for 1.8 to 5.8 $\mu\text{g/ml}$ of Pd(II); the colour is stable for 15 days and Sandell's sensitivity is 8.3 ng/cm^2 . Platinum interferes but Mn(II), Zn, Cd(II), Fe(III), Ni(II) and Co(II) can be masked by using EDTA to four-fold excess. A 500-fold excess of F^- , Cl^- , Br^- , I^- , NO_3^- , oxalate, $\text{S}_2\text{O}_3^{2-}$, SCN^- , acetate, SO_4^{2-} , citrate, tartrate or EDTA can be tolerated. Vanadium(V), Mo(VI), W(VI), Th(IV), Cr(III), Ca(II), Mg(II), Ba(II), Al(III) do not interfere with the method.	37

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref.
2'-Hydroxy-3',5'-dimethyl-azobenzene-4-sulphonic acid (DMHAS)	470 nm $\epsilon=4160$	3.5	The reagent in more than five-fold excess rapidly forms a 1:2 (Pd:R) chelate with Pd (II) at pH 3.5. The pH is adjusted with aq. NaOH or HClO_4 and the absorbance is measured. The optimum analytical range is 1.7 to 9.2 ppm and Beer's law is obeyed from 0.45 to 10.0 ppm. Sandell's sensitivity is $0.037 \mu\text{g}/\text{cm}^2$. Silver(I), Hg(II), Os(VIII), and Ru(III) interfere seriously in the determination of Pd while Pt(IV), Rh(III), Fe(III), Fe(II), Ni(II) and Co(II) do not interfere. Copper(II) has also been determined with the reagent and forms 1:2 complex (Cu:R) at pH 8.0. the absorbance is measured at 480 nm for Cu and the optimum analytical range is 0.9 to 5.2 ppm. Sandell's sensitivity is $0.013 \mu\text{g}/\text{cm}^2$. Bivalent Fe, Fe(III), Cr(III) and Zn interfere seriously.	38

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
6-Carboxyl-6'-hydroxyl-3',5'-dichloroazobenzene-4-sulphonic [2-(3,5-dichloro-2-hydroxyphenylazo)-5-sulphobenzole] acid	550 nm $\epsilon=7000$	0.5-1.0	The reagent in 4 to 6-fold excess forms instantaneously a 1:1 complex with Pd(II) at pH 0.5 to 1 and the absorbance is measured. The optimum ranges for determination are 1.3 to 10.3 ppm for Pd. Sandell's sensitivity is 0.026 $\mu\text{g}/\text{cm}^2$ for Pd. The reagent has also been used for Ni(II) and Cu(II). It forms a 1:1 complex with Cu(II) at pH 4 to 7 and a 1:2 (Ni:R) complex with Ni at pH 7.5 to 7.8. The absorption maxima are at 510 nm for Cu(II) and 500 nm for Ni(II). The optimum ranges (ppm) are 1.1 to 5.8 for Cu and 0.9 to 5.0 for Ni. Sandell's sensitivity ($\mu\text{g}/\text{cm}^2$) is 0.013 for Cu and 0.01 for Ni.	39

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Isonitrosobenzoyl acetone [2-hydroxyimino-1-phenyl butane-1,3-dione]	415 nm $\epsilon=11430$	< 1.5	A 0.1% solution of this reagent in benzene extracts Pd quantitatively from aq. solution at pH < 1.5 and from media of 0.5 to 4M H_2SO_4 , 1 to 2N HNO_3 or 1 to 4N-acetic acid. The absorbance of the Pd-reagent complex is measured and the colour is stable for 24 h. The calibration graph is rectilinear for 0.5 to 15 $\mu g/ml$ of Pd, and the optimum analytical range is 5 to 150 μg in 50 ml. The error is $\pm 3\%$ for 56 μg . No interference is caused by metals normally associated with Pd. Chloride, Br^- , I^- , SCN^- , CN^- , thiourea and EDTA hinder the extraction of Pd into benzene, but their effects are controllable.	40
1-Benzoyl-3-(2-pyridyl)- 2-thiourea	350 nm $\epsilon=10500$	1.4-4.6	An ethanolic 1% solution of the reagent forms with Pd at 250, in 0.08 to 1.6M-HCl medium, a dark brown 1:1 complex which is extricated from aq. medium (pH 1.4 to 4.6) into ethanol- $CHCl_3$ (1:3) for determination of 1.18 to 9.44 $\mu g/ml$ of Pd. Sandell's sensitivity is 0.01 $\mu g/cm^2$.	41

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
8-Hydroxy 2-methylquinoline	425 nm $\epsilon=6644$	1.0-5.0	An aliquot (1 ml) of PdCl_2 test solution (containing 188.8 μg of Pd) is mixed with sufficient buffer solution to maintain the volume of the aq. phase at 10 ml and at optimum pH 1 to 5. Then a solution (1 ml) of the reagent in acetone is added. The ppt. formed is extracted into CHCl_3 (10 ml), followed by washing of the aq. phase with CHCl_3 (2x5 ml). The extract and washings are then diluted with CHCl_3 to 25 ml, and the absorbance of this solution is measured. Beer's law is obeyed over the range 1 to 10 $\mu\text{g}/\text{ml}$ of Pd. There is no interference from Pt(IV), Rh, Ni(II), Cr(III), U(VI), Al, Be, Ce(III), Pb(II) or Ti(III). There is serious interference from Mn(II), Cd, Hg(II), Zn, Os(VIII) and Ru(III).	42

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Phenyl-2-pyridyl ketone azine	425 nm 450 nm	1.5-3.0	The reagent forms a yellow 1:1 complex with Pd at pH 1.5 to 3 after heating for 30 min. at 50° to 70°. An ethanolic 0.05% solution of the reagent is used and pH is adjusted with 1M H ₂ SO ₄ . The optimum analytical range is 1.6 to 8.9 ppm at 425 nm and 2.2 to 5.6 ppm at 450 nm, corresponding mean errors being ± 0.6 and $\pm 0.9\%$, respectively. Rh(III), Os(VII) and Ru(IV) do not interfere; in concentration up to twice that of Pd, but Cu, Ni, Bi, Hg(II) and S ₂ O ₃ ²⁻ interfere seriously in concn. equal to that of Pd. The method has been applied to some industrial analysis and to chalcocopyrite.	43

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Monothiourea-3-nitro phthalic acid [2-nitro-6-(thioureidocarbonyl) benzoic acid]	306 nm $\epsilon=29000$	Acidic (HCl)	The sample solution, made 0.5M in HCl, is extracted with a 0.5 mM solution of the reagent in CHCl_3 -pentanol (2:1) and the absorbance of the combined extracts is measured against a reagent blank. Beer's law is obeyed over the range 0.1 to 3 $\mu\text{g}/\text{ml}$ of Pd, Os(IV), Co, Hg(II), Ru(II), Pt(IV), V(V), Fe(III) and Ag do not interfere.	44
5-d ethylamino-2-nitrosophenol	486 nm $\epsilon=43800$	2-3M H_2SO_4	The reagent gives a 1:2 (Pd:R) complex with Pd(II) in 2 to 3M H_2SO_4 extracted in CHCl_3 and the absorbance is measured. Excess of the reagent is removed by washing the CHCl_3 extract with 2.5M H_2SO_4 . The calibration graph is rectilinear for 0 to 20 μM Pd. Iodine gives strong negative interference, as does $> 5 \mu\text{M}$ Os(VIII), Pt(IV), Zr(IV), Rh(III) or Br. The method has been applied to various catalysts with good recovery of added Pd.	45

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Picolinaldehyde-2-quinolythydrazone	250 nm	2.5	Palladium reacts with the reagent at pH 2.5 to form a 1:1 complex. The complex is formed in 1 hour when reagent concentration is ≈ 0.1 mM. Beer's law is obeyed for 4 to 20 ppm of Pd(II) and the error in Pd determination is 1%; however, Fe(II), Fe(III), V(V) and Ti(IV) interfere.	46
1,5-Bis(2-chlorophenyl)-3-(phenylcarbamoyl)formazan (I)	640 nm $\epsilon=10400$	3.5	The reagents serve as photometric reagents for palladium. Both are sensitive and selective for Pd; (I) reacts only slowly in dioxan-H ₂ O at pH 3.5 to give a green 1:2 (Pd:R) chelate. Reagent (II) is soluble in H ₂ O and at pH 3 reacts quickly on warming to give a similar complex. The detection limit with (II) is 0.02 $\mu\text{g/ml}$ of Pd. Interference by other precious metals is only serious at ratios (relative to Pd) of 100:1 but Cu interferes at 5:1.	47
Di- α -naphthylamine salt of 1,5-bis-(2-chloro-5-sulphophenyl)-3-(phenylcarbamoyl)formazan (II)	633 nm $\epsilon=115000$	3.0		

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5-Pyridylazobenzene-2,4-diamine (PADAT)	≈ 590 nm $\epsilon=35000$	Weakly acidic or neutral	The reagent forms a red purple 1:1 complex in a weakly acidic or neutral medium. The Pd complex is extracted into benzene and absorbance is measured. The sensitivity is 3 ng/cm^2 of Pd.	48
Bulaprazine maleate	490 nm $\epsilon=3500$	1.3-2.2	The reagent forms a red 1:1 complex with Pd(II) in HCl-Na acetate buffer medium that exhibits λ max between 482 and 500 nm. A 6-fold excess of the reagent relative to Pd is required. At 490 nm, Beer's law is obeyed for 0.2 to 17.0 $\mu\text{g/ml}$ of Pd(II). In the determination of 8 $\mu\text{g/ml}$ of Pd(II), there is negligible interference from the following species at the concentration ($\mu\text{g/ml}$) shown in parentheses: $\text{S}_2\text{O}_3^{2-}$ (0.1), Au(III) or Ce(IV) (0.2), I $^-$ (0.3), Fe(II) (0.8), Ru(III) (1), Rh(III) (4), Ir(III) (5), Os(VIII) (8) and Pt(IV) (10).	49

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thio [anti] pyrine [2, 3-dimethyl-1-phenyl-pyrazoline-5-thione] (I)	330 nm $\epsilon=37000$	3-1M HCl	The reagent (I) forms a 1:4 Pd(II):R complex in aq. media 0.3 to 1M in HCl and containing a ≈ 10 -fold molar excess of (I) relative to Pd. Beer's law is obeyed for 0.1 to 3 $\mu\text{g}/\text{ml}$ of Pd. The coefficient of variation is $< 0.9\%$ (7 results) when determining 36 μg of Pd.	50
Bis-(thioantipyrinyl) methane and 1,1-Bis-(thioantipyrinyl)butane			Platinum (II) has also been determined with this reagent. A 1:4 (Pt:R) complex is formed in aq. media 0.3 to 1M in HCl. The Pt complex exhibits maximum absorption at 335 nm ($\epsilon=13,500$) and Beer's law is obeyed for 0.8 to 14 $\mu\text{g}/\text{ml}$ of Pt. Up to 10,000-fold amounts of Zn, Al, Mn(II), Co, Ni or Ga; 5000-fold amounts of Cd and 2500-fold amounts of Ti (relative to Pd) or 4000-fold amounts of Zn or Al; 2000-fold amounts of Mn(II) or Ga; 400-fold amounts of Ni or Co; 100-fold amounts of Ti and 2-fold amounts of Cu (relative to Pt), do not interfere.	

Name of the Reagent:	λ max. or working wavelength with ϵ	pH	Remarks	Ref's.
5-Chloromethyl-4-selenahexahydropyrimidine-2-thione	340 nm	1.0-9.0	The reagent forms a 1:2 (Pd:R) Pd-complex that is stable over the pH range 1 to 9 and obeys Beer's law for 1 to 2.7 $\mu\text{g/ml}$ of Pd. Although Au(II), Fe(III), Pt(IV) and U(IV) interfere with the complex forming reaction, Al, Th, In, La, Ce, Bi, Pb, Sn, Hg and Zn do not.	51
p-Nitrosodiphenylamine sulphonic acid (I)	535 nm ($\epsilon=4800$)	2.0-3.5	Reagent (I) shows max. absorbance at 435 nm and it forms a water soluble complex with Pd at pH 2.0 to 3.5 with maximum absorption at 535 nm.	52
p-Nitrosophenyl-1-naphthylamine (II)	510 nm ($\epsilon=4200$)		Reagent (II) gives a complex with Pd with λ max at 510 nm. Gold interferes with (I), but up to 200 ppm, may be present when using (II).	

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1-Cyclohexyl 3,4,6-trimethyl-1H,4H-pyrimidine-2-thiol (I)	390 nm ($\epsilon=3100$)	1 to 10M HCl	The reagents (I) and (II) form yellow complexes with Pd in a medium 1 to 10M in HCl. The complexes can be extracted into CHCl_3 for spectrophotometry at 390 and 420 nm, respectively. The analytical ranges are 6 to 34 ppm of Pd with (I) and 4.2 to 13.3 ppm with (II). Iodine, thiourea and $\text{S}_2\text{O}_3^{2-}$ interfere.	53
1-Phenacyl 4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol (II)	420 nm ($\epsilon=4000$)	1 to 10M		
1-Benzylindazolin-3-one	400 nm ($\epsilon=2000$)	6.0	The reagent reacts with Pd to form a yellow 1:3 (Pd:R) complex suitable for spectrophotometry. To a 1.1 to 2.2 mM solution of PdCl_2 in HCl are added acetate buffer solution (pH 6) and 1 ml of alcoholic 21% reagent. The resulting yellow complex is extracted into CHCl_3 , and the absorbance of the extract is measured against a CHCl_3 buffer solution. Beer's law is obeyed for 0 to 70 $\mu\text{g/ml}$ of Pd, Fe(II) and Cu(II) interfere. The method has been used to determine Pd in catalysts and in Pd-thiocaprolactam complexes.	54

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3-(2-Hydroxy-5-methyl phenyl)-5-(p-methoxy phenyl) isoxazoline [2-[5-(4-methoxyphenyl)-2-isoxazolin-3-yl]-p-cresol)	332 nm	2.0	To an aliquot containing $\approx 46 \mu\text{g}$ of P.d) of a stock solution, water is added and the pH is adjusted to 2.0 with 0.1M HClO ₄ or NaOH, and the solution is made up to 10 ml. This solution is allowed to equilibrate with 10 ml of a 1.3 mM solution of the reagent in isobutyl alcohol for ≈ 10 min, then the absorbance vs the yellow organic phase is measured against a reagent blank. Beer's law is obeyed for 1.0 to 20.0 $\mu\text{g/ml}$ for Pd.	55

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Pyridyl-2-thienyl- β -ketoxime	433 nm	6.0	Determination of trace amounts of palladium in a noble metal-bearing sulphide concentrate without pre-concentration is reported. After decomposition of the sample with HCl-HNO ₃ , the Pd in a dil. HCl medium is converted into its 1:2 complex with the reagent formed at pH 6. The presence of Na ₂ (EDTA) or citrate serve as masking agents for base metals and Au(III). The complex is then extracted into CHCl ₃ . The extract is washed with dil. HCl and the organic phase is made up to a known volume for measurement of the absorbance against CHCl ₃ . A reagent blank is treated similarly and the concentration of Pd is obtained from the rectilinear calibration graph (0.2 to 2 ppm). Analysis of a standard concentrate gave a value of 0.35 oz/ton compared to a certified value of 0.37 oz/ton. The method replaces the tedious fire-assay wet chemical procedures.	56

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Di(2-quinolyll)ketone -2-pyridyl hydrazone	624 nm	1.0-6.0	The sample solution containing 5 to 120 μg of Pd is diluted with H_2O to ≈ 40 ml; the pH is adjusted to 2 with aq. NaOH or HCl, and after addition of 5 ml of ethanolic 0.1% reagent, the solution is set aside for 10 min. It is extracted by shaking with two 10 ml portions of CHCl_3 for 30s and 10s, respectively. The extract is diluted to 25 ml and dried over Na_2SO_4 . The absorbance of the extract is measured against CHCl_3 . Readings are constant over the pH range 1 to 6. Beer's law is obeyed for 0.25 to 5.0 ppm of Pd in the CHCl_3 extract and for concentration from 1.1 to 2.6 ppm. The standard deviation is ± 0.02 to 0.04 ppm. In the determination of 54.8 μg of Pd, 5 mg of Fe(III) could be masked with 1 ml of a saturated citrate solution; Cu(III), Ni, Sn(II) and I^- interfere.	57

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Crystal violet (C.I. Basic Violet 3)	582 nm	0.6 (SCN ⁻) 0.9 (I ⁻)	Palladium(II) is extracted into benzene, as the Pd(II) -SCN ⁻ crystal violet 1:3:1 complex, from H ₂ SO ₄ medium of pH 0.6 that is 0.6 mM in KSCN and 14 μ M in reagent. Similarly a Pd(II) - I ⁻ - crystal violet 1:3:1 complex is extracted at pH 0.9 from aq. phase 1.6 mM in KI and 7 μ M in reagent. Both complexes exhibit λ_{max} at 582 nm., and Beer's law is obeyed for 0.02 to 1.8 μ g/ml or 0.17 to 1.4 μ g/ml, respectively, of Pd. The colour is stable for 12 h if the extract is mixed (5:2) with acetone. A one-fold excess (relative to Pd) of Pt, Ir, Os, Ru and Rh does not interfere for the complex with SCN ⁻ and a 5-fold excess of Os, Ru and Rh and an equivalent amount of Pt and Ir do not interfere for the complex with I ⁻ . The method has been used for determining Pd in mixtures of platinumoids.	58

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Mercaptobenzothiazole (I)	440 nm $\epsilon=2200$	2.5-5.5	Palladium(II) is separated from 1000-fold amounts of Pt(IV), Ir(IV) or Rh(III) by extracting the Pd-2-mercapto-benzothiazole (I) (1:2) complex into CCl_4 from acetate buffered medium (pH 2.5 to 5.5) 0.4M in NaClO_4 and 2mM in (I). Beer's law is obeyed for 2 to 100 $\mu\text{g/ml}$ of Pd. When a method based on these facts is used to determine $\approx 0.17\%$ of Pd in a platinum wire also containing $\approx 6\%$ of Ir, $\approx 5\%$ of Rh and $\approx 1\%$ of Ag, the coefficient of variation is 8.2% (10 results). 2-Mercaptobenzoxazole forms a similar complex with Pd(II) exhibiting λ max at 294 nm, but Pt, Rh and Ir interfere.	59
2-Mercaptobenzoxazole (II)	294 nm $\epsilon=34000$			

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Triphenyl phosphine (TPP)	346 nm $\epsilon=22600$	1 to 6M HCl	The test solution is made 1 to 6M in HCl, and extracted with TPP solution in benzene. The absorbance of the extract is measured. A 20-fold excess of any other Pt group metal or transition metal does not interfere. Palladium can be determined in presence of 5 mg/ml of Pt. The method has been used to determine down to 10 ppm of Pd in Pt-based samples.	60
Isonitrosobenzoyl acetone (2-hydroxyimino-1-phenyl butane-1,3-dione)	405 nm $\epsilon=10200$	0.5M acetic acid	Palladium (10 to 130 μg) is extracted from 0.5M acetic acid medium into a 0.1% solution of the reagent in benzene. The extract is diluted to 10 ml, and the absorbance of the yellow 1:2 complex is measured. Beer's law is obeyed over the given range, and equivalent amounts of Au, Pt(IV), Ru and Os(VIII) are tolerated but W(VI) and V(V) interfere. Ruthenium(III) has also been determined with this reagent. the orange-red Ru complex (20 to 120 μg of Ru) is formed at pH 3.5 to 4.5 by heating at 100°	61

for 3 min. with an ethanolic 3% solution of the reagent. The complex is extracted into isobutyl methyl ketone and its absorbance is measured at 470 nm ($\epsilon=5400$). Iron, Pt and Pd interfere.

62

Isonitrosodibenzoyl methane 420 nm 35
(1,3-diphenyl-propanetrione
-2-oxime)

To 10 to 95 μg of Pd(II), 1 ml of ethanolic 0.05% reagent is added. The pH is adjusted to 3.5 in a total volume of 25 ml. This is extracted with 10 ml of benzene and the absorbance of the extract is measured against a reagent blank. Beer's law is obeyed for 1 to 9.5 $\mu\text{g/ml}$ of Pd. The complex is stable for at least 48 h, the standard deviation is 0.0015 and determination can be carried out in the presence of Fe, Co, Ni, Pt, Os, Ir, Cu, Au and Se. Ruthenium(III) has also been determined with the reagent at pH 4.5 and the absorbance of CHCl_3 extract is measured at 530 nm. Beer's law is obeyed for 1 to 12 $\mu\text{g/ml}$ of Ru.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4,4'-Bis(dimethylamino)-thiobenzophenone	520 nm $\epsilon=130000$	2.8	Extraction-photometric determination of traces of palladium, found in silver and copper metals, crude copper and anode slime, with the reagent is reported. A solution containing up to 3 μg of Pd is treated with 10 ml of 0.5M HBr - 5M H_2SO_4 (1:1), diluted to 50 ml with H_2O and shaken for 5 min., with 5 ml of 15% trioctylamine solution in toluene. The organic phase, containing the bromo complex of Pd with trioctylamine is washed for 2 min. with 20 ml of 0.1M HBr - 0.5M HClO_4 , and the aqueous phase is discarded. The organic phase is treated with a 0.01% solution of the reagent in butanol, and shaken with 50 ml of 1M Na acetate buffer. The absorbance of the organic phase is measured against the trioctylamine solution. Beer's law is obeyed for up to 3 μg of Pd. The recovery of Pd is quantitative, and down to 0.1 μg could be determined.	63

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Hydroxy-1-naphthal-doxime	402 nm $\epsilon=10000$	0.05 to 3M H_2SO_4	To the sample solution containing up to 100 μg of Pd are added 2 ml of 0.05M zephramine and 10 ml of 1M H_2SO_4 . The solution is diluted to 20 ml with H_2O , and the acidity is adjusted to 0.5M with H_2SO_4 ; then 10 ml of 0.01M reagent in $CHCl_3$ is added, the mixture is shaken and the phases are separated and centrifuged. A 1:2 (Pd:R) complex of Pd with the reagent is formed, which can be quantitatively extracted into $CHCl_3$ from 0.05 to 3M- H_2SO_4 , and the absorbance is measured. Beer's law is obeyed for up to 100 μg of Pd and the sensitivity is 9.7 ng/cm^2 of Pd for 0.001 absorbance. For the determination of 53.0 μg of Pd, the standard deviation and coefficient of variation are 6.7 ng and 1.34% respectively. There is serious interference from Mo(VI) and Os(III).	64

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thio-2-thenoyl trifluoroacetone [1,1,1-trifluoro-4-mercapto-4-(2-thienyl)but-3-en-2-one]	410 nm ($\epsilon=37000$)	5.8	A solution containing < 30 μg of Pd is adjusted to pH 5.8 with acetate buffer solution and is diluted to 50 ml with H_2O , and 10 ml of a 0.21 mM solution of the reagent in xylene is added to form the complex. The organic phase is washed with 10 ml of $\text{Na}_2\text{B}_4\text{O}_7$ -NaOH buffer solution (pH 11.5) and the absorbance of the organic phase is then measured against a reagent blank. Beer's law is obeyed for up to 30 μg of Pd and the coefficient of variation for the determination of 20 μg of Pd is 0.5%. There is interference from Cu(II) , CN^- and S^{2-} when present in amounts 10% of that of Pd.	65
Hexadecyl trimethyl ammonium bromide (I) and o-Hydroxyquinolphthalain i.e. 2',3',6',7'-tetrahydroxy spiro [iso benzofuran-1 (3H),9'-[9] xanthen] -3-one (II)	625 nm ($\epsilon=127000$)	4.7-5.5	In the presence of an excess of non-ionic surfactant, Pd forms a blue 2:2:3 complex with reagent (I) and reagent (II). The sample solution (containing 1 to 6 μg of Pd) is mixed with 1 ml of 0.5% methyl-cellulose solution, 1.5 ml of 1mM (I), 2 ml of Walpole acetate buffer solution (pH 5.0) and 5.0 ml of	66

methanolic 1mM (II). The mixture is diluted to 10 ml with H₂O, the solution is maintained to 60° for 30 min and the absorbance is measured. The complex is very stable in aq. solution at pH 4.7 to 5.5, and the calibration graph is: rectilinear. There is interference from Fe(II), Cu(II), Al and Cr(III) but Cu(III) and Al can be masked by citric acid.

67

The test solution containing 75 to 25 µg of Pd(II) is treated with 5 ml of a 0.1% solution of the reagent in aq. 40% dimethyl formamide, 8 ml of dimethylformamide and 5 ml of 0.5M-KNO₃. The mixture is diluted to 25 ml with H₂O, and the absorbance is measured at 480 nm after 30 min. Alternatively, the complex can be extracted into CHCl₃, the absorbance of the dried (Na₂SO₄) extract is measured at 500 nm.

480 nm
500 nm

Piccolinald=hyde-4-
nitrophenyl hydrazone

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Quinoline-2-aldehyde thiosemicarbazone (QAT)	510 nm $\epsilon=2500$	1M HCl	To a solution containing 50 to 200 μg of Pd(II) and 0.01% QAT solution in aq. 50% dithionite (4 ml), HCl is added to give 10 ml of a 1M-solution. The complex is extracted into isobutyl methyl ketone (2:5 ml) and the absorbance is measured. Beer's law is obeyed for the given range. Co^{2+} , Pb(II) and SCN^- interfere seriously. The method has been applied to the analysis of steels and a nickel-silver sample. The reagent has also been used for the determination of nickel (iii). The pH is adjusted to 7.5 and the yellow complex formed is extracted into CHCl_3 (2.5 ml) and the absorbance is measured at 460 nm ($\epsilon=1580$). Cadmium(II) and Pb (II) interfere.	68

Dl(2-pyridyl)glyoxal- 2-quinolyl hydrazone	470 nm $\epsilon=5000$ 570 nm $\epsilon=10,800$	8.0-11.0 2.0-6.5	In aq. 50% ethanol, this reagent forms with palladium a yellow 1:2 (Pd:R) complex at pH 8 to 11 and a red 1:1 complex at pH 2 to 6.5. Palladium between 10 to 74 μg (80 μg for the red complex) is determined (10 ml) with the reagent of concentration 0.1mM. The maximum error is $\pm 1\%$. Beer's law is obeyed in this range. The corresponding Sandell sensitivities are 0.007 and 0.009 $\mu\text{g}/\text{cm}^2$. The method has been successfully applied to solutions simulating those of alloy, and containing 6 ppm of Pd and 4 ppm of Cu or Ag or 6 ppm of Au.	69
5-Methoxy-2-nitrosophenol	510 nm $\epsilon=430000$	2M H_2SO_4	In 2M H_2SO_4 medium (final vol. 10 ml), this reagent (1 ml of ethanolic 0.1% solution) forms with Pd, an orange-red 1:2 (Pd:R) complex. The complex is extracted into CHCl_3 and absorbance is measured against a reagent blank. The calibration graph is rectilinear for the range 25 to 250 μg of Pd in the extract. Sandell's sensitivity is 24 ng/cm^2 . Tin(II) and Ag(I) interfere seriously and must be absent.	70

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thiocaprolactam	400nm	Acidic	The reagent forms a ternary complex with Pd(II) in aq. acid medium containing Cl^- , Br^- or I^- . The complex is readily soluble in CHCl_3 and is used for the determination of Pd. Beer's law is obeyed for 1 to 20 $\mu\text{g}/\text{ml}$ of Pd. The complex is stable for 12 h. By this method, palladium is determined on an alumina catalyst after its dissolution, addition of KI, extraction with 5 ml of 1% reagent solution in CHCl_3 and dilution of the extract to 10 ml with CHCl_3 . Tervalent Au, Pt(IV), Bi(III), Hg(II), Ag and Cu(II) interfere.	71
3-Bromo-2-hydroxy-4-methoxy-5-methylbenzoic acid	390nm	1.0-3.0	Palladium(II) is extracted from ClO_4^- medium of pH 1 to 3 by a 2mM solution of the reagent in isobutyl alcohol and the absorbance is measured. Beer's law is obeyed for 3 to 30 $\mu\text{g}/\text{ml}$ of Pd(II) in the organic phase. Zirconyl(II) and EDTA interfere. Sandell's sensitivity is 33 ng/cm^2 .	72

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Salicylaldehyde hydrazone (α -hydrazono-o- cresol)	425nm $\epsilon=5300$	3.0-5.0	This reagent forms a 1:2 (Pd:R) complex with Pd II in a medium of 75% acetone at pH 3 to 5. The 1:2 complex is extracted into CHCl_3 for spectrophotometry. Beer's law is obeyed for up to 21 ppm of Pd. Sandell's sensitivity is 20 ng/cm^2 . Os (VIII) has also been determined with this reagent. A 1:1 complex is formed at pH 9.5 to 10 in a medium containing 30% of acetone and 20% of dimethylformamide. The absorbance is measured at 430 nm. Sandell's sensitivity is 60 ng/cm^2 ($\epsilon = 3200$).	73

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
3-(2'-Thiazolylazo)2,6-diamino toluene	590 nm $\epsilon=53500$	1.0-2.5M perchloric acid	This reagent gives coloured complexes with Co, Cu and Pd. The reagent forms with Pd (II) a 1:1 (Pd:R) blue chelate, which is soluble in perchloric acid of up to 5-6 M. The 1.0-2.5 concentration is used as Cu(II) and Co(II) complexes are not formed at this concentration. For determination of Pd 10 mg of sample (e.g., catalyst or dental gold) is dissolved in HClO_4 . HCl , aqua regia or EDTA solution and diluted to 100 ml. To a suitable aliquot, 2 to 8 ml of 60% HClO_4 is added and the absorbance is measured after 30 min. Beer's law is obeyed between 0.1 and 1.9 ppm. There is interference by SCN^- and I^- and by > 20-fold amounts (relative to Pd) of Os(IV) or Ir(IV).	74
1,5-D phenylcarbazone in dodecyl sulphate (I)	560nm $\epsilon=17,000$	1.5-4.4	Palladium reacts with the reagent to form a red fish-violet complex, which can be	75

hexadecyl trimethyl ammonium bromide(II)	(i) 460 nm $\epsilon=23000$ (ii) 630 nm	2.3-5.5	retained in aq. solution by the addition of dodecyl sulphate in the pH range 1.5 to 4.4 (λ max at 560 nm). Alternatively, hexadecyl trimethyl ammonium bromide has also been used to retain the complex in aq. solution at pH 2.3 to 5.5 (λ max at 460 and 630 nm). The complex can also be extracted at pH 2.0 to 4.4 (λ max at 480 nm and 620 nm) into isobutyl methylketone. The palladium to ligand ratio is 1:2 in all instances.	76
Isobutyl methyl ketone (III)	(i) 430 nm (ii) 620 nm $\epsilon=48000$	2.0-4.4		
Thiophen-2-carbohydrazide	395 nm	1.3	This reagent reacts with Pd to form a 1:1 complex exhibiting λ max at 390 to 410 nm, depending on pH. To the test solution containing 40 to 140 ppm of Pd(II), 6 ml of 10 mM reagent and buffer solution of pH 1.3 are added. The solution is diluted to 25 ml with H_2O , and the absorbance of the complex is measured against a reagent blank.	

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs
Sodium 4,8 - diamino-1,5-dihydroxy-9,10-dioxoanthracene-2,6-disulphonate	720 m μ ($\epsilon=4370$)	10.5	The reagent reacts with Pd(II) to form a 1:1 complex. To a sample containing 4 to 20 ppm of Pd(II), 10 ml of aq. 2.109 mM reagent and 20 ml of Na ₂ CO ₃ -NaHCO ₃ buffer solution (pH 10.5) are added. The solution is diluted to 50 ml with H ₂ O, and the absorbance is measured against a reagent blank. Beer's law is obeyed for 4.8 to 18.2 ppm.	77
Amminopentacyanoferrate and nitroso-R salt	705nm	5.0	To the Pd(II) solution, containing 5 ml of 0.01M Fe(NH ₃) (CN) ₅ ³⁻ and 1 ml of acetic acid ammonium acetate buffer solution (pH 5) is added and the solution is diluted to 40 ml. After 15 min, 5 ml of aq. 0.05N-nitroso-R salt is added and the solution is diluted to 50 ml and mixed. After 30 min, the absorbance of the solution is measured against a reagent blank. Beer's law is valid in the concentration range 0.01 to 1.2 ppm of Pd, Fe(III), Fe(II), Au(III) and Ag interfere. Platinum could be tolerated in 10-fold amounts relative to Pd(II).	78

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1-(2-Pyridylazo)-2-naphthol	600nm	5.5	The reagent is used for determining Pd and Ni in thin films of resistor alloys in glass-ceramic substrates. The film is dissolved in HCl-HNO ₃ (1:3). The pH of an aliquot containing 1 to 10 μ g of Ni and 10 to 50 μ g of Pd is adjusted to 2 with aq. NH ₃ , then hexamine, Na acetate buffer solution of pH 5.5, reagent and acetone are added and the absorbance is measured at 562 nm (for Ni plus Pd) and 600 nm (for Pd alone). The Ni is determined by difference.	79
2'-Hydroxy-3,5'-dimethylacetophenone oxime	400nm $\epsilon=1030$		Palladium reacts with the reagent to form a 1:2 water insoluble complex, which is extracted into CHCl ₃ to give a yellow solution. The stability constant of the complex is 3.05×10^7 . Beer's law is obeyed for 2 to 70 ppm of Pd. Sandell's sensitivity is 0.010 μ g/cm ² . The error is $\pm 0.5\%$ for 5.0 to 43.0 mg of Pd.	80

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
N-Butyl thiopicolinaldehyde (I)	361nm $\epsilon=76800$ 400nm $\epsilon=48000$	0-8.5	Extraction of 10μ M-Pd at pH 0 to 8.5 is 9%. The ϵ values of the reagent at 361 and 400nm are 62,400 and 41,500 respectively and the corresponding values for the Pd-(I) ₂ complexes are 76,800 and 48,000. Comparable concentration of Au(III) and Pt(IV) did not affect the extraction of Pd(II).	81
Trans-1,2-diaminocyclohexane tetraacetate	340 nm $\epsilon=10000$	5.0-6.0	The reagent, in at least a 10-fold molar excess (relative to Pd), forms in acetate buffer solution (optimum pH 5 to 6), a 1:1 metal-to-ligand complex. Beer's law is obeyed for 10 to 80 μ g/ml of Pd(II). Amounts of other species (relative to Pd) that can be tolerated are Ir(III) 3, Rh(III) 1, Pt(IV) 0.5 and Ni(II) or Co(II) 10. Iron(III) and Cu(II) interfere.	82

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Ethylene bis (diphenyl phosphine) monoxide	340nm $\epsilon=14000$	1M HCl	The reagent (in sixfold molar excess) reacts with Pd(II) and forms in aq. 50% ethanol (1M in HCl), a 1:4 (Pd:R) complex that is extractable into CHCl_3 . Beer's law is obeyed for ≈ 1 to 7 $\mu\text{g}/\text{ml}$ of Pd. Tolerable amounts of other metals relative to Pd are Cu 25,000, Co or Ni 1000, Pt 15 and Ir 10. Rhodium (III) has also been determined with this reagent. A 1:5 [Rh(III):R] complex is produced in presence of > 15 fold molar excess of reagent and if it is heated at 100° for 30 min. The complex as extracted into CFCl_3 exhibits λ max at 325 nm ($\epsilon = 9500$). The method has been used for the determination of Pd(12 to 65 μg) and Rh(58 to 102 μg) in a single sample. Pd is initially extracted and determined. The aq. phase is heated with additional reagent, and Rh is extracted and determined.	83

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Dimethylformamide (I) and Michler's thioketone [4,4'-bis(dimethylamino) thiobenzophenone] (II)	530nm $\epsilon=300000$	2.0-3.0	In aq. 35% dimethylformamide (I) at pH 2 to 3 (acetate buffer) that is 0.1mM in reagent, a Pd(II)-(I) (1:4:2) complex is produced. Beer's law is obeyed for 0.05 to 0.25 $\mu\text{g/ml}$ of Pd. Strong oxidants, Au(III), Hg(II) and Pt(II) interfere. This method has been used for the determination of 0.11% Pd in a catalyst based on MnO_2 , the coefficient of variation is < 3% (five results). The Mn(IV) is reduced initially to Mn(II) with hydroxylamine.	84

5-(2-Hydroxy-3,5-dinitrophenylazo) quinolin-8-ol-1-oxide

530 nm
ε=21100

1 to 3M
HNO₃

The reagent forms a 1:1 complex with Pd(II) in a medium of aq. 50% acetone that is 1 to 3M in HNO₃. A 4-fold molar excess of the reagent relative to Pd is needed, and the reactants are heated together at 65° for 20 min. Beer's law is obeyed for 0.3 to 3 μg/ml of Pd. The colour is stable for 12 h, and the complex is extracted into toluene. Tolerable amounts of other species (relative to Pd) are Mg and Ag 5000; Mn, Al, Ni, Zn, Pb, Bi, La, Ce(III), Y, SO₄²⁻, F⁻ oxalate, citrate and tartrate 2000; Pt 430; W(VI) and Co 120; Au and Mo(VI) 100; Cu, Cr(III) and Zr(30); Fe (III) and Cl⁻ 20; EDTA 2; and Ti(IV) 1500 (if masked with tartrate). Vanadium(V), Cr(VI) and H₂O₂ interfere. A method based on these findings is used to determine 0.01 to 2% of Pd in Ni-Pd, Mg-Ni-Pd and Mg-Ag-Pd alloys, samples being decomposed by HNO₃-H₂O (1:1). The coefficients of variation are < 13% (5 to 7 results).

Name of the Reagent:	λ_{max} or working wavelength with ϵ	pH	R:marks	Refs.
2-Hydroxy-1-naphthal- doxime	402nm	1M H ₂ SO ₄	Determination of palladium, present in palladium brazing filter metal, with the reagent is reported. The sample (0.1g) is dissolved by heating it with 10 ml of HNO ₃ , the solution is diluted to 100 ml with H ₂ O, and an aliquot (containing up to 100 μ g) of Pd) is treated with 2 ml of 0.05M zephiramine and 10 ml of 1 M H ₂ SO ₄ . This mixture is diluted to 20 ml with H ₂ O and shaken for 10 min. with 10 ml of 0.01M reagent in CHCl ₃ . The absorbance of the separated organic phase is measured against a reagent blank.	86
Phthalazinohydrazones of Picolinaldehyde (i) Quinaldalddehyde (ii) Benzothiazol-2-one (iii)	537nm 580nm 587nm	-0.5M H ₂ SO ₄	For determinations with (i) or (iii), the sample solution containing < 65 μ g of Pd (ii), 1 ml of 12M H ₂ SO ₄ and 4 ml of aqueous 1mM reagent are shaken with H ₂ O (10 ml) and CHCl ₃ (10ml), and the absorbance of the CHCl ₃ extract is measured at the	87

respective wave length. For the determination with (III), 0.5 ml of 1M-NaCl is also added, the complex is extracted with 10 ml of the reagent (0.25 mM in CHCl_3) and the absorbance is measured.

Palladium (II) forms a green 1:1:3 complex with pyrogallol red (0.02mM) and hexadecyl trimethyl ammonium bromide (0.1 to 0.4 mM) at 25° and pH 3.4 (0.2M acetate buffer). After 30 min, the absorbance of the complex is measured. Beer's law is obeyed for 0.05 to 6.8 ppm of Pd. The mean error is $\pm 0.6\%$ and the coefficient of variation is 1.1%. Sandell's sensitivity is $0.003 \mu\text{g}/\text{cm}^2$. Bivalent Cu, Zr(IV), Ta(V), VO(II), $\text{UO}_2(\text{II})$ and ClO_4^- interfere. The 1:1:3 Pd complex with (I) and (II) is also formed at pH 7.2 (phosphate buffer solution) but is less suitable for measurements.

Pyrogallol red (I) and
hexadecyl trimethyl
ammonium bromide (II)

640nm 3.4

88

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thionalide [2-mercapto-N-(2-naphthyl)acetamide]	375nm	Acidic	Concentration and photometric determination of palladium in minerals and ores is reported. The sample (50 g) is fused at 1200° with 50 g of PbO, 5 g of starch, 80 g of Na ₂ CO ₃ (containing 0.15 g of AgNO ₃), 30 g of borax and 30 g of glass. After 45 min. 10 g of PbO, 5 g of borax, 5 g of Na ₂ CO ₃ and 1 g of starch are added, and fusion is continued for a further 15 min. The product is cupelled in a MgO crucible at 1100°, and the silver button obtained is dissolved in 5 ml of HNO ₃ . After 1 h, 15 ml of HCl is added and, after another ~ 1 hr, the solution is heated on a water bath for 1 h, cooled, mixed with 10 ml of HCl and diluted to 50 ml with H ₂ O. This is solution A. A portion of solution A is mixed with 10 ml of H ₂ O, 1 ml of 50% tartaric acid solution and 1 ml of ethanolic 1% reagent. After ~10 min, the Pd complex is extracted into 10 ml of a benzene (or toluene)-isobutyl alcohol mixture (7:3), and the absorbance of the extract is measured. The limit of detection is 50 ppb.	89

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Furaldehyde thio-semicarbazone	364nm	6.0	A sample of palladium coating is cleaned with hot dimethylformamide and then dissolved by heating in minimum volume of HNO_3 (1:1). The solution is diluted with H_2O to contain 20 to 100 $\mu\text{g}/\text{ml}$ of Pd. To a portion of this solution containing 20 to 100 μg of Pd, 5 ml of acetate NH_3 buffer solution (pH 6), 1.5 ml of 10% EDTA solution, 1 ml of 0.2M $\text{Na}_2\text{S}_2\text{O}_3$, 2.5 ml of ethanol and 10 ml of 0.6 mM solution of the reagent in ethanol are added. The mixture is maintained at 60° for 30 min, then diluted to 25 ml with H_2O . The absorbance is measured against a metal blank which does not contain $\text{Na}_2\text{S}_2\text{O}_3$ and reagent solutions with the rest of the conditions identical. Beer's law is valid in the concentration range studied.	90

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Lumomagne: on 15-(5-chloro-2-hydroxy-3-sulpho-	485 nm	3.0-8.0	A portion of the powdered sample (e.g. a catalyst) containing <0.8 mg of Pd is heated with 5 ml each of HNO_3, H_2O and conc. HF. The solution is evaporated to dryness. The treatment is repeated twice, the final residue is dissolved in 5 ml of hot HCl and the solution is made up to 50 ml with H_2O. A portion of solution containing 4 to 32 μg of Pd is mixed with 1 ml of saturated NaF solution, sufficient aqueous NaOH to raise the pH 3 to 8, 3 ml of acetate buffer solution (pH 3.8) and 2 ml of aq. 0.2% reagent. The mixture is heated for = 5 min at 60° to 100°, cooled, mixed with 2 ml of 2% diphenylguanidine solution in 0.1M HCl and made up to 15 ml with H_2O. A 20 ml portion of this solution is extracted with 5 ml of butanol, and the absorbance of the extract is measured against a reagent blank extract. No interference is caused by 200-fold amounts of Hg(II), 10-fold amounts of Pt(IV), Ru or Au, 5-fold amounts of Ni or Co, 3-fold amounts of Rh(III) or equal amounts of Fe(III) or Cu.	91

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Pyrogallol red (I)	600nm $\epsilon=14000$	6.5	A mixture of 0.2 mM reagent (I) (30 ml), phosphate buffer solution of pH 6.5 (10 ml) and sample solution is diluted to 50 ml with H_2O and after ≈ 70 min. the absorbance of the red Pd(II) complex is measured against a reagent blank. Beer's law is obeyed over the range 0.4 to 2.2 $\mu g/ml$ of Pd(II). Improved sensitivity and more rapid colour development are attained in the presence of 1-ethoxycarbonyl pentadecyl trimethyl ammonium bromide (II). To the sample solution, acetate buffer solution of pH 5.5 (10 ml) 0.2 mM reagent (I) (15 ml) and 5 mM (II) (5 ml) are added. The volume is brought to 50 ml with H_2O and after ≈ 20 min. the absorbance at 620 nm ($\epsilon = 26000$) of the purple blue Pd(II)-(II) complex is measured against a reagent blank. Beer's law is obeyed over the range 0.2 to 3.7 $\mu g/ml$ of Pd(II). Many cations are tolerated, but Au, Fe(III), Fe(II), Cu, Al and Pb interfere in both methods	92

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Succinic acid monothioamide [4-oxo-4-thio-undecylobutyric acid]	295nm $\epsilon=30000$	Acidic	The reagent, as a 0.01% solution in water, ethanol or propanol, forms a yellow complex with Pd(II) in acid medium with absorption maxima at 230 to 240 nm and at 295 m μ . The test solution is mixed with 5 ml of 5M-HCl and 15 ml of the reagent solution, the mixture is diluted to 50 ml with water, and after 5 min, the absorbance is measured. Beer's law is obeyed for 0.5 to 4 μ g./ml. of Pd, Bivalent Fe, Sb(III), Cu(II), Bi(III), Sn(III) and Pt(IV) interfere. A 500-fold amount (relative to Pd) of EDTA; a 200-fold amount of Zn, Ni, Mg or Cd; a 100-fold amount of Hg(II), Pb(II), Co or Mn(II); a 50-fold amount of Cr(III) or a 10-fold amount of Sn(II), Al, Ir(III) does not interfere.	93

Name of the Reagen:	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Methopromazine maleate	585 nm $\epsilon=14000$	Acidic	The reagent forms, in acid medium, an orange 1:1 complex and a violet 1:2 complex with Pd(III). The violet complex is stable for 3 h and exhibits λ_{max} at 595 nm, and is used for determining 1 to 8 $\mu\text{g/ml}$ of Pd in H_3PO_4 medium. The coefficient of variation is < 1% for the concentration range of Pd cited. Au(III), V(V), Cr(VI), Os(VIII), Pt(IV) and Rh(III) interfere.	94

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3'-Bromo-2'-hydroxy-5'-methyl acetophenone oxime (BHAMO)	400nm $\epsilon=1000$	-2.5	Palladium(II) forms a yellow 1:2 (Pd:R) complex with the reagent. The pH of the sample solution, containing 20 to 50 μ g of metal ion, is adjusted to -2.5, and a sixfold excess of the reagent is added. After 5 min, the precipitated complex is extracted into CHCl ₃ (3x5 ml). The extracts are combined and diluted to 25 ml with CHCl ₃ and the absorbance is measured. Beer's law is obeyed for 7.42 ppm to 51.94 ppm of Pd(II), Fe(II), VO(II), UO ₂ (II) and VO ₂ ⁺ 3 interfere seriously. For determination of copper(II), nickel(II) and cobalt(II) with the reagent the pH is adjusted to 5.5, 6.5 and 7.5 respectively, and the absorbance is measured at 640, 600 and 400 nm respectively. The reagent forms 1:2 complex ²³ with these metal ions. Beer's law is obeyed for 8.64 ppm, 5.87 to 52.83 ppm and 3.6 to 54.0 ppm of Cu(II), Ni(II) and Co(II) respectively. The corresponding ϵ values are 170, 84, and 640 respectively.	95

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Phenanthrenequinone monosemicarbazone	470nm	5.0-7.0	Palladium(II) forms a 1:2 (Pd:R) complex with the reagent. The Pd complex is formed instantaneously in aqueous solution and is extracted at pH 5 to 7 into CHCl_3 . Beer's law is obeyed for 0.2 to 19.2 $\mu\text{g/ml}$ of Pd. Sandell's sensitivity is 19 ng/cm^2 . There is serious interference from Co, Ni, Cu, Ru(III) and Cd. Rhodium has also been determined with the reagent. A 1:3 (Rh:R) insoluble Rh complex is formed at pH 7.2 to 8.8 by heating on a water bath for 2h. The complex is dissolved by adding dimethylformamide such that its final concentration is 70% (V/V). The absorbance is measured at 480 nm. Beer's law is obeyed for 0 to 16.5 $\mu\text{g/ml}$ of Rh. Sandell's sensitivity is 18 ng/cm^2 . There is interference from Fe(III), Os(VIII), Ir(III), Pt(IV) and >2 $\mu\text{g/ml}$ of Ru(III).	96

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Solochrome red B [C.I. Mordant Red 9]	655nm $\epsilon=12057$	6.0	The test solution, containing 275 to 1250 μg of Pd(II) is treated with 6.5 ml of 2 mM reagent and 10 ml of acetate buffer solution of pH 6. The solution is boiled gently, cooled and 2 ml of 0.05M-EDTA is added to mask Co, Ni, In, Pt and Th. The solution is diluted to 25 ml and the absorbance is measured at 655 nm. For the determination of 2.5 to 25 μg or 25 to 275 μg of Pd, 2.5 or 3 ml of reagent is added, and the absorbance is measured at 488 or 548 nm respectively, where the composition is reported to be 1:1. Beer's law is obeyed in the studied range 50 to 11, 11 to 1 and 1 to 0.1 ppm of Pd(II) at 655, 548 and 488 nm respectively using blank and water references. The interference study is made under optimum conditions and absorbance is measured at 488 nm. Na, K and Fe(III) do not interfere. Rh(III), Ti(II), $\text{UO}_2(\text{II})$ and Zr(IV) ions cause moderate interference in molar ratios to Pd(II) of 8.2, 22.2, 31.6 and 21.4 respectively. Cr(III) and Au(III) ions interfere strongly.	97

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref.
Isonitrosoethyl benzoyl acetate [ethyl benzoyl hydroxyimino acetate]	410nm	4.0	The test solution (20 ml) containing 10 to 110 μg of Pd is mixed with 2 ml of ethanolic 0.2% reagent. The pH is adjusted to 4.0 with NaOH solution and HCl. The mixture is made up to 25 ml and shaken for 1 min with 10 ml of CHCl_3 and the absorbance of the extract is measured against a reagent blank. Ruthenium (200 μg) does not interfere, while Rh(III), ascorbate, SCN^- interfere. Ru(III) has also been determined with this reagent. The pH is adjusted to 5 and absorbance of the extract is measured at 500 nm. Palladium (200 μg) does not interfere. Sn(II), Fe(III), Zr, Th, ascorbate and EDTA interfere with analysis for R ₁ .	98

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
p-Chloro and p-bromo benzoyl acetone oxime	400nm	3.5	Palladium forms a yellow 1:2 (Pd:R) complex with an ethanolic 0.1% solution of either of the reagents. The complex is extracted from slightly ethanolic aq. 20 ml solution (pH 3.5) into CHCl_3 (10 ml) and absorbance is measured. Beer's law is obeyed for 109 to 100 μg of Pd. The coefficient of variation ranges from 4 to 1% for 10 to 40 μg of Pd. Recoveries of Pd from mixtures with ions with which they are commonly associated are > 99%. There is serious interference from Zr, EDTA, SCN^- and oxalate as well as from Te(IV) , Fe(III) , Sn(II) , Cr(III) , Os(VIII) and ascorbate in the determination of Pd. Ruthenium (III) has also been determined and forms an orange red complex at pH 5. After heating for 10 min. at $\sim 95^\circ$ it is extracted into ethyl acetate (10 ml) and absorbance is measured at 475 nm. Beer's law is obeyed for 20 to 200 μg of Ru. The coefficient of variation ranges from 3 to 0.75% for 40 to 120 μg of Ru (six determinations).	99

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Mercaptobenzo thiazole	440nm	5.0	Determination of palladium(II) from solutions containing lead(II) and silver(I) with the reagent is reported. A solution containing 0.02M $\text{Pb}(\text{NO}_3)_2$, 0.138M AgNO_3 and 1.75mM PdCl_2 is mixed with 2M NaClO_4 , acetate buffer solution (pH 5) and 0.02M-reagent. Palladium complex is extracted with CCl_4 and the absorbance of the organic phase is measured. Beer's law is obeyed in the range 0.2 $\mu\text{g/ml}$ to 0.1 mg/ml of Pd. The method has been applied to the analysis of natural ores (Ag content = 0.65 mg in a 50 g sample) after dissolution in HNO_3 .	100
Pyridine-2-aldehyde [picolinaldehyde] -2-pyridyl hydrazone	360nm 390nm	5.0	The reagent forms a 1:1 complex with Pd(II) at an optimum pH of 5. The absorbance of the complex at 360 or 390 nm is practically linearly related to Pd concentration from 1 to 8 ppm. In the determination of 7 ppm of Pd, interference is caused by > 2 ppm of Ag, Cu(II), Co, Sn(II), Ni, Fe, V(V) and Au(III).	101

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2,2'-pyridyl bis-(2-quinolyl hydrazone) (PB ₂ QF)	550nm $\epsilon=12800$	3.5-6.6	Beer's law is obeyed for up to 9.5 ppm of Pd and the optimum working range is 1.06 to 8.5 ppm. Sandell's sensitivity is 8.2 ng/cm ² . The reagent is used to determine Pd in solutions simulating the composition of Pd alloys. There is no interference from other Pt-group metals.	102
Di-(2-pyridyl) ketone 2-quinolyl hydrazone	570nm $\epsilon=14000$	4.5-7.5	Palladium forms a 1:1 violet complex with the reagent. It is extracted from a solution of pH 4.5 to 7.5 into CHCl ₃ , and the absorbance of the organic phase is measured. Beer's law is obeyed for up to 10.64 ppm of Pd. Sandell's sensitivity is 7.6 ng/cm ² of Pd.	103

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref's.
[Dl(2-pyridyl)methylidene hydrazinol benzene [Dl-(2-pyridyl)ketone phenyl hydrazone]	500nm	0.5-0.1N NaOH	Palladium(II) forms a 1:1 yellow orange complex with the reagent in 0.5 to 0.1N-NaOH; Beer's law is obeyed for up to 5.32 ppm of Pd(II). By this method, Pd(II) has been determined in a synthetic solution of composition corresponding to jewellery alloy.	104
Sodium 6-(4-amino-1, 2,4-triazol-3-ylazo)-4-hydroxy-naphthalene-1-sulphonate (i) Green complex (ii) Red complex	670nm $\epsilon=7000$ 540nm $\epsilon=12000$	Acidic Neutral or alkaline	Palladium(II) forms two water soluble complexes with the reagent - a green complex in strongly acidic medium (λ max 670 nm) and a red one in neutral or alkaline medium (λ max 540 nm). Both complexes are stable and obey Beer's law.	105

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1-Nitroso-2-naphthol	410 to 413nm	1.0-2.0	Determination of platinum and palladium in a CaO based sorbent is reported. The sorbent is dissolved in aqua regia, the solution is repeatedly evaporated to dryness with HCl, and the solution of the residue is filtered. For the determination of Pd, the filtrate is diluted with H ₂ O and treated with EDTA; then the solution is adjusted to pH 1 to 2, aq. reagent is added and the solution is left for 10 min. The complex is extracted into toluene. The excess of reagent is removed with 1M NaOH, and the absorbance of the Pd-reagent complex is measured. For the determination of Pt, the filtrate is treated with 1M Sn(II) in 3.5M HCl and the absorbance is measured at 440 nm.	106
Rhodamine 6G [C.I. Base Red 1]	530nm	2.5	A flotation spectrophotometric method for determining palladium by means of the ion-association complex of pentabromopalladate (II) with the reagent is reported. To the sample solution containing < 8 μ g of Pd are added aq. 10% KBr (8 ml) and 1mM reagent (2.5 ml). The solution is adjusted to	107

pH 2.5 with 0.1M HCl and is diluted to 25 ml with H₂O. Benzene (10 ml) is added as flotation agent, and, after shaking the mixture for 45 sec., the aq. phase is removed and the benzene phase (containing the complex) is washed with H₂O (3x10 ml). The ppt. is filtered off and dissolved in 25 ml of dimethylformamide, and the absorbance of this solution is measured against a reagent blank. Beer's law is obeyed for up to 0.3 µg/ml of Pd and the coefficient of variation (7 determinations) ranges from 2.6% for 8 µg of Pd to 7.5% for 1 µg of Pd. Platinum, Rh, Ir, Hg, Mo, Cd, Au, Bi, Ga and Mn interfere. The method has been applied to the determination of Pd in high purity platinum after double precipitation of Pd with dimethylglyoxime with Ni as scavenger. In the determination of 4.60 µg of Pd in a 50 mg sample the standard deviation is ± 0.2 µg. The selectivity of the method is poor but its sensitivity is better than that of other methods.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Dithizone and methyl trioctyl ammonium chloride	530 nm	9.6M-HCl	To a solution (in 9.6 M-HCl) containing up to 20 μ g of Pd(II) is added 10 ml of a solution (in CHCl_3 containing 10 ppm of dithizone and 5% of methyl trioctyl ammonium chloride. The mixture is shaken for 5 min. After 2 h, the absorbance of the organic phase is measured against a reagent blank. The sensitivity is 6 ng/cm ² of Pd(II).	108

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Methionineprazine hydrochloride (MMH)	480nm	1.4	Simultaneous determination of palladium (II) and gold(III) with the reagent is described. The stoichiometric ratio of the orange red Pd-MMH complex is found to be 1:1. The sample solution is treated with HCl-Na acetate buffer (5 ml) of pH 1.4 and 5 ml of 0.5% reagent solution is added and then made up to 25 ml and mixed. The absorbance is measured at 480 nm for Pd or at 630 nm for Au. The two elements have been determined in the same solution by use of simultaneous equations. Beer's law is obeyed for 0.4 to 21 ppm of Pd(II) and 0.2 to 10 ppm of Au(III). Sandell's sensitivity is 30 ng/cm ² for Pd(II) and 14.3 ng/cm ² for gold(III). Iodine, thiosulphate, EDTA, Ru(III), Os(VIII), Fe(III), W(VI), Rh(III), Ir(III) and Pt(IV) interfere seriously.	109

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thiocyanate and methylene blue	660nm $\epsilon=170000$	2.5	Flotation spectrophotometric determination of palladium with thiocyanate and methylene blue is discussed. To a solution containing up to 12 μg of Pd, 2 ml of 0.25M KSCN is added and diluted to 20 ml. The pH is adjusted to 2.5 with dil. HCl and 2 ml of 1 mM methylene blue is added. The ion pair complex formed is floated by shaking the solution for 45 sec. with 10 ml of benzene, and the aq. phase is discarded. The ppt and benzene phase are washed with H_2O (3x10 ml), the benzene is discarded. The separated ion-pair compound is dissolved in 25 ml of acetone, and the absorbance of the solution is measured. The molar ratio of Pd to methylene blue in the ion associate is 1:2. Beer's law is obeyed in the Pd concentration range 0.03 to 0.5 $\mu\text{g}/\text{ml}$. Serious interference is caused by Ag, Pb, Mo, Bi and W. The method has been applied to the determination of Pd in high purity silver with preliminary extraction of Pd as the dimethyl glyoxime complex.	110

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs
Chrome Azurol SIC I, Mordant Blue 29, and hexadecyltrimethyl ammonium ions	630nm $\epsilon=88000$	3.8-5.0	Palladium(II) forms a ternary complex with chrome Azurol SIC I and hexadecyl trimethyl ammonium ions(II) in aq. acetate buffer medium of pH 3.8 to 5 containing 0.002% of (I) and 0.01% of (II). Beer's law is obeyed for 0.2 to 0.8 $\mu\text{g}/\text{ml}$ of Pd. Tolerable amounts of diverse metals relative to Pd are Mg and Cd 100%, Tl(III) 40%, Zn, and Mn 100%; La and Pb 50; Hg(II), Y, Sn(IV), Cr(III), Mo, Co and Ni 10 and Bi and W 1. Copper, Be, Al, Ga, Sc, Ti(IV), Zr, Bi, V(IV) and Fe(III) interfere; but Sn(II) has been masked with NH_4F . The method is used to determine ≈ 0.1 to 0.3 g/l of Pd (II) in an activation solution, containing H_2PdCl_4 and SnCl_2 , used in the production of printed-circuit boards. The coefficient of variation is < 30% (six results). Similar ternary complexes of Cu, Fe(III), V(IV), Ti(IV) and Zr are also studied.	111

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
6-Aminoquinoline-2 3-dithiol (AQDT)	570nm $\epsilon=41000$	2.0	Separation and determination of palladium and platinum with the reagent is discussed. Palladium(II) forms a 21:2 complex (Pd: AQDT) with the reagent. To the test solution containing 5 to 20 μg of Pd, 5 ml of 0.05% solution of the reagent is added. The solution is adjusted to pH 2.0 with dil. HCl and extracted with isoamyl alcohol (2x5 ml). The combined extracts are dried with anhydrous Na_2SO_4 and diluted to 10 ml with isoamyl alcohol and the absorbance is measured against a reagent blank. Beer's law is obeyed for up to 2.5 ppm for Pd. Sandell's sensitivity is 0.0025 $\mu\text{g}/\text{cm}^2$. For the separation and determination of Pd and Pt, the test solution containing Pd and Pt is heated on a water bath with 1 ml of 1.77 mM-SnCl ₂ and to the cooled solution reagent solution is added (5 ml of 0.05%). The solution is adjusted to pH 2.5 and then extracted with isoamyl alcohol (2x5 ml). The absorbance of the organic phase is	112

measured at 570 nm. The aq. phase is then collected and re-adjusted to Ph 0.5 and extracted with isoamyl alcohol (2x5 ml) and dried with anhydrous Na_2SO_4 and diluted to 10 ml with isoamyl alcohol. The absorbance of 1:2 (Pt-AQDT) complex is measured at 640 nm for Pt. The molar absorptivity of the Pt complex is 78000 and Sandell's sensitivity is 0.0024 $\mu\text{g}/\text{cm}^2$.

113

The reagent (7) forms a 1:1 complex with $\text{Pd}(\text{SCN})_3\text{H}_2\text{O}^-$ in an aq medium, 0.18M in H_2SO_4 , 80 mM in KSCN and 17 μM in (1). This complex can be extracted into m-xylene, toluene or benzene. The extract is washed thrice with 0.1M H_2SC_4 and the absorbance is measured. Beer's law is obeyed for 0.02 to 1.8 $\mu\text{g}/\text{ml}$ of Pd. Tolerable amounts of metals relative to Pd are: 50-fold excess of Fe, Cd, Ni, Co, Cu and Sn; and 10-fold excess of Pt, Ir, Rh, Os and Ru.

Acidic
(H_2SO_4)

597 nm

Brilliant green [C.I.
Basic Green 1]

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
4-S-Benzyl-1-(4-chlorophenyl)-5-phenyl-2,4-dithioisobutiret (BPPTB) in presence of stannous chloride	355nm	0.5	Determination of copper, rhodium, palladium and platinum with the reagent in the presence of stannous chloride has been reported. For the separation and determination of Pd(II) and Cu(II), the test solution, containing 10 to 100 μg of Pd and 2 to 30 μg of Cu, is adjusted to pH 0.5 and extracted with a 1 mM solution of the reagent in isoamyl alcohol. The absorbance of the organic phase containing Pd(II) is measured at 355 nm. Copper (II) is determined by adjusting the aq. phase to pH 4.2 with NaOH and extracting it with chloroform; the absorbance of the CHCl_3 phase is measured at 368nm. For the separation of Pd(II), Pt(IV) and Rh(III), the test solution containing 10 to 100, 20 to 100 and 10 to 50 μg of the respective species is adjusted to pH 0.5 and extracted with the solution of the reagent in isoamyl alcohol and Pd is determined as discussed. The aq. phase is made 3.5M in HCl, 0.1M in SnCl_2 and extracted with 1 mM reagent in CHCl_3 (10 ml). The absorbance of the organic phase	114

containing Pt(IV) is measured at 407nm. The residual phase is made 1.6M in HCl and 0.1M in SnCl₂ and heated at 90° for 1 h. After cooling, the solution is thrice extracted with 1mM-reagent in CHCl₃. The absorbance of the Rh(III) complex is then measured at 375 nm. Procedure for the simultaneous determination of Pd, Rh and Cu in binary mixtures has also been reported.

5,5-Methylene-bis (salicylic acid)

335nm

115

For the determination of Pd, the reactants are heated for 1 h at 90°, then the mixture is cooled, and the absorbance is measured. Beer's law is obeyed for 2 to 9 ppm of Pd. Tartrate, acetate, NO₃⁻, Cl⁻, As(V), Cd, Mn(II), Zn, Ca, Sr, Ba, Mg, Na, K and Li in amounts up to 100 ppm do not interfere with the determination of 7.5 ppm of Pd whereas 3ppm of Hg(II), Sb(III), Sn(II), Bi(III), Au(III), Mo(VI), Cu(II), Fe(III), Al, Ga, Ce(III), Ce(IV), Th(IV), Th, In or CrO₄²⁻ interfere.

Name of the Reagen :	λ max. or working wavelength with ϵ	pH	Remarks	Refs
2-Furaldehyde-2-pyridyl hydrazone	430 nm	9.85	A method is reported for determining 0.5 to 2 ppm of Pd(II). A complex of Pd(II) with the reagent is formed in borate buffered medium of pH 9.85 containing 60% of ethanol. Copper(II), Ag, Co(II), Ni(II), Zn, Hg(II), Tl(III), Au(III), Rh(III) and Ce(IV) in the pH range 3 to 11 also react with the reagent. The structure and spectrophotometric parameters of the complex have also been discussed.	116
1,1-Dimethyl-3-(4-phenyl-2-thiazolyl)thiourea	390 nm $\epsilon=38500$		Palladium(II) reacts with the reagent to form a 1:2 (Pd:R) complex which is extracted into CHCl_3 and the absorbance is measured. The excess of the reagent is removed by washing the CHCl_3 extract with 0.1M NaOH. The optimum conc. range for the determination is 0.59 to 1.93 $\mu\text{g/ml}$ of Pd. The method has been successfully applied to the determination of Pd in palladised asbestos.	117

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5,10,15,20-Tetrakis-(4 sulphophenyl)porphine (TPPS ₄)	412 nm $\epsilon=220000$		To a solution containing up to 7.5 μg of Pd(II), 1 ml of acetate buffer solution of pH 4.5, ≈ 10 ml of H ₂ O and 3 ml of 1 μM TPPS ₄ are added. The mixture is heated for 15 min in a boiling water bath. The cooled solution is treated with 1.5 ml of 1 M chloroacetic acid and H ₂ O is added to make up 25 ml, and the absorbance is measured against a reagent blank. Copper interferes seriously. Up to 100 μg of Mg, Ca, Ni, Co, Cd, Pb, Cr(III) or Pt(IV); 10 μg of Fe(III), Ti(IV) or Mn(II); or 1 μg of Al or Zn affect the absorbance value for 5 μg of Pd in 25 ml of solution by < 5%.	118

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3'-Bromo-2'-hydroxy-5'-methyl acetophenone hydrazone	400nm ($\epsilon=4500$)	2.5-5.0	To a solution containing 25 to 60 μg of Pd (II), an excess of solution of the reagent in acetone at pH 2.5 to 5 is added. The complex formed is extracted into CHCl_3 , and the absorbance of the extract is measured. Beer's law is obeyed over the range 3.8 to 27.3 ppm of Pd(II). Thiourea, SO_3^{2-} , SCN^- , EDTA, Cu(II) and Fe(III) interfere seriously; Cu(II) and Fe(III) could be masked by tartrate. The method is successfully applied in the determination of Pd(II) in alloys and jewellery.	119

2,6-Diamino-3-(2'-thiazolylozo) benzene [4-(2-thiazolylozo)-m-phenylene diamine]	585 nm	Acidic (HClO ₄)	The same solution containing 2.5 to 37.5 µg of Pd(II) (as perchlorate) is mixed with 2 ml of 1mM solution of the reagent in 1M HClO ₄ and diluted to 25 ml with H ₂ O. After 30 min. the absorbance of the solution is measured against a reagent blank. Beer's law is obeyed for 0.1 to 1.5 ppm of Pd. The relative error is = 0.24%. Interference is caused by SCN ⁻ , Br ⁻ , I ⁻ , Ir(IV), Ru(III) and Pt(IV). The method has been used for the analysis of Pd-bearing catalysts.	120
1-(1-Naphthyl)-4,4,6-trimethyl-1H, 4H-pyrimidine-2-thiol (NTPT)	430nm	Strongly Acidic	The reagent forms a CHCl ₃ extractable yellow complex (λ max 430 nm) with Pd(II) in strongly acidic medium. The metal to ligand ratio is 1:2. At least 70 to 80-fold amounts of transition metals and of other Pt group metals relative to Pd do not interfere. Osmium(IV) has also been determined with the reagent. The reagent forms a blue 1:2 [Os(IV):R] complex with Os(IV) which exhibits λ max at 590 nm.	121

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(Thiazolylazo)resorcinol	540nm $\epsilon=30200$	5.0	Determination of rhodium and palladium with the reagent is reported in the presence of cation active tartrates. Palladium(II) forms a ternary complex with 1 mM and a 5 mM solution of hexadecyl pyridinium bromide (micelle form) at pH 5 and 25°. The pH is adjusted with 0.2M acetate buffer and the measurements are made against a reagent blank. The analytical range is 0.5 to 3.2 $\mu\text{g/ml}$ of Pd. The ratio of Pd to any other metal of Pt group must be > 4:1. Cl ⁻ in concentration > 0.2M interferes. Rhodium (III) has also been determined and forms a ternary complex with 1mM reagent and a 5mM solution of hexadecyl pyridinium bromide (micelle form) at pH 5.6 and $\approx 100^\circ$ (15 min. heating). The pH is adjusted with 0.2M acetate buffer and the absorbance is measured at 545 nm for Rh ($\epsilon=37500$). The analytical range is 0.5 to 3.6 $\mu\text{g/ml}$ of Rh.	122

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
N-4-Chlorophenyl benzohydroxamic acid	430 nm	3.0	The reagent (0.01% solution in chloroform- zene) forms an orange complex with Pd(II) at pH 3.0. The organic phase is separated and dried and the absorbance is measured. Sensitivity is enhanced by addition of 0.001% dithizone solution, and a violet complex is formed that is measured at 520 nm. Beer's law is obeyed for 10.5 to 84 ppm or 2.5 to 30 ppm of Pd for the complexes formed in the absence and presence of dithizone respectively.	123

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Chrome Azurol S [C.I. Mordant Blue 29] (I)	620nm	-5	Palladium forms a ternary complex with the reagent and cetyl trimethyl ammonium bromide (centrimide) (II) and cetyl pyridinium bromide(III). The green complexes between Pd, the dye(I) and either of the surfactants (II or III respectively) are formed at pH -5 (0.2M acetate buffer) and have the composition Pd(I)(II)_2 and Pd(I)(III)_2 . Beer's law is obeyed in the range 0.05 to 2.98 ppm of Pd at 25°. Sandell's sensitivity is 2 ng/cm ² . The mean error is $\pm$ 0.5% for $\approx 12 \mu\text{M}$ Pd. Perchlorate, Ru(III) and Zr(IV) interfere seriously, but can be removed initially.	124
2-(5-Chloro-2-pyridylazo)-5-dimethyl aminoaniline	610nm $\epsilon=81000$	0.6M HCl	Beer's law is obeyed for 0.1 to 1.4 ppm of Pd. Copper(II), Co(II) and Ni(II) also react with the reagent in the presence of Na dodecyl sulphate and form a 1:3 (M:R) complex. The complexes of Cu(II), Co(II) and Ni(II) exhibit λ max at 535 nm (at pH 7; $\epsilon=65,000$); 615	125

nm (in 2.4 HCl; $\epsilon = 110,000$) and 570 nm (at pH 6; $\epsilon = 114,000$) respectively. Beer's law is obeyed for 0 to 0.6 ppm of Cu, 0 to 0.5 ppm of Co and 0.05 to 0.5 ppm of Ni.

126

The method is based on catalysis by Pd(II) of the reaction of NaH_2PO_2 with molybdate to produce a 'molybdenum blue'. The test solution of PdCl_2 in 0.1M HCl (5 ml), maintained at $24^\circ \pm 1.5^\circ$, is mixed with 10 ml of 20% NaH_2PO_2 solution followed at once by 10 ml of 4% $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ solution simultaneously with initiation of a timing device. After 5 min., a portion of the solution is transferred to a 2 cm-cell and the absorbance is measured at 1-min. intervals to give the rate of change of absorbance with time. Beer's law is obeyed for concentration of Pd between 0.055 and 0.11 $\mu\text{g/ml}$. There is no interference from NH_4Cl or Zn(II) or from small amounts of Pd(IV), Co(III), Fe(III), Hg(II) or SCN^- .

Acidic

650nm

NaH_2PO_2 and molybdate:

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref's.
Nitroso-R salt	520 nm $\epsilon=15,400$	Acid c	Determination of palladium in titanium alloys with the reagent is reported. The sample, 0.25 g containing 0.04 to 0.8% of Pd is dissolved in 20 ml of H_2SO_4 (1:1) with subsequent dropwise addition of HNO_3 and HCl (3 to 4 ml of each). The solution is evaporated to fumes and the cooled residue is dissolved in H_2O to 100 ml. An aliquot (10 ml) is treated with 5 ml of HNO_3 (1:1), 2 ml each of acetic (1:1) and 1% reagent solution, and H_2O to make up 50 ml. The absorbance is measured, after a few minutes, against a reagent blank. Beer's law is obeyed for up to 4 $\mu g/ml$ of Pd. Variations in temp. have little effect and the colour is stable for several days. In the 50 ml solution, there is no interference from ≤ 1 mg of Ag, Al, Fe, $Mn(II)$, $Mo(VI)$, $Cu(II)$, Zn, Ni, Co, $Sn(IV)$, $Cr(III)$, Zr, Nb, Ta W or V.V) or 25 mg of Ti.	127

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Ethylenediamine solutions	400 to 440nm	Acidic	These samples are solutions containing, typically: PdCl_2 (2g/l), amines (28 ml/l of ethylene diamine) and hypophosphite: e.g. 10 g/l of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$. A test portion (10 ml) is mixed with 1 ml of CuSO_4 solution (0.4 g/l) as catalyst and 20 ml of alkaline NaClO (67 g/l; pH 12 to 13) to oxidise the hypophosphite and the amine. After 5 min. unconserved NaClO is decomposed by addition of conc. HCl (10 ml) and the free Cl_2 is removed by the addition of pieces of marble.	128

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Michler's thio ketone [4,4'-bis (dimethylamino thiobenzophenone)]	540 nm	~3	Determination of trace amounts of Pd, Pt, Cu, Ag, Au or Hg in alloys, minerals, catalysts, natural waters and effluents by complex formation with the reagent is reported. The sample is mixed with acetate buffer solution (pH = 3) in dimethylformamide, the trace metal is complexed by adding the reagent solution (1mM) in dimethylformamide, and the absorbance of the complex is measured. Reducing and oxidizing agents interfere but Cl^- , Br^- , SC_4^{2-} , acetate and EDTA are tolerated. Possible mutual interference of the previous metals is indicated. Limits of detection are $25 \mu\text{g/l}$.	129

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Nitroso-1-naphthol	550nm	1.5-3.5	The sample containing <25 μg of Pd is diluted to 30 ml with water, and 3% EDTA solution (2 ml) is added. The pH of the solution is adjusted to 1.5 to 3.5 and ethanolic 1% reagent solution (0.1 ml) is added. After 10 min, the Pd complex is extracted into CHCl_3 (10 ml) and the absorbance of the extract is measured. There is no interference from Cu or Fe(II) (in 1000-fold amounts relative to Pd); Ni, Cr(VI) or Mo(VI) (in 100-fold amounts); or Co(II) (in 30-fold amounts). The complex is stable for 3 h, and the limit of detection is 0.06 mg/l of Pd. By this method, palladium is determined in industrial waters.	130

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Phenanthraquinone monothiosemicarbazone	600nm $\epsilon=2200$	Acidic (acetic acid)	To 10 ml of solution containing 25 to 180 μg of Pd, 2 ml of 0.01% solution of the reagent in dimethylformamide containing 1M acetic acid is added. The 1:2 (Pd:R) complex is formed which is extracted into CHCl_3 (2x5ml). The extract is combined and dried with anhydrous Na_2SO_4 and the absorbance for Pd is measured against a reagent blank. Beer's law is obeyed over the concentration range of 25 μg of Pd. The coefficient of variation is 1.5% for Pd(100 μg). Sandell's sensitivity is 0.04 $\mu\text{g}/\text{cm}^2$. Cadmium interferes most seriously. In the determination of 100 μg of Pd 3 mg of Ru could be tolerated. Ruthenium(III) has also been determined with the reagent and forms a 1:1 (Ru:R) complex with the reagent. To 10 ml of solution containing 10 to 150 μg of Ru, 4 ml of 0.06% reagent in DMF and	131

acetic acid (2M) is added. The mixture is heated in a boiling water bath for 10 min, cooled and extracted with CHCl_3 (2x5ml). The extracts are combined and dried with Na_2SO_4 and the absorbance of the green complex is measured at 600 nm ($\epsilon=4740$) against a reagent blank. Beer's law is obeyed over the concentration range of 10 to 150 μg of Ru/ 10 ml of organic phase. The coefficient of variation is 1.2% for Ru(50 μg). Sandell's sensitivity is 0.02 $\mu\text{g/cm}^2$. In the determination of 50 μg of Ru, 10 μg of Pd is tolerated.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1,5-Dibenzylidene-3-thiocarbohydrazide (DBTCH)	370nm $\epsilon=42680$	5.8-6.8	Simultaneous determination of palladium (III) and platinum (IV) with the reagent is reported. Palladium forms a yellow coloured complex with DBTCH at room temperature while platinum forms a complex after heating over a boiling water bath for at least 30 min. The test solution containing 6 to 65 μg of Pd(III) and 10 to 175 μg of Pt(IV) in 20 ml, is adjusted to pH 5.8 to 6.8 and mixed with 2 to 3 ml of ethanol and 2 ml of a 1.4 mM ethanolic solution of the	132

reagent. After 2 h at room temperature the solution is extracted with ethyl acetate (5x5ml). The extract is dried and made up to 25 ml with ethyl acetate, and Pd is determined by measuring the absorbance against a reagent blank. Pt remains in the aqueous phase and its absorbance is measured at 370 nm against reagent blank. The colour formed by either metal is stable for ≥ 24 h. The composition of both Pd(II) and Pt(IV) DBTCH complexes is found to be 1:2 (M:R). Beer's law is obeyed for 0.2 to 3 ppm of Pd or 0.5 to 7 ppm of Pt. The corresponding Sandell sensitivities are 0.0025 and 0.0065 $\mu\text{g}/\text{cm}^2$ for Pd(II) and Pt(IV) respectively.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Rubeanic acid [dithio oxamide] in presence of Piperidine	380nm $\epsilon=6246$	Slightly acidic	Determination of palladium with rubeanic acid in the presence of piperidine, quinoline, α -picoline or collidine is reported. To a slightly acidic solution containing Pd, 2 ml of piperidine, 5 ml of quinoline, 3 ml of α -picoline or 2 ml of collidine and 1 ml of 0.1% dithio-oxamide solution in aq. 95% ethanol are added. The mixture is diluted to 25 ml with anhydrous ethanol, and the absorbance of the solution is measured at 380nm (piperidine or quinoline) or 410 nm (α -picoline or collidine). With pyridine and collidine a 1:1 (Pd:Rubeanic acid) ratio is observed	133
Quinoline	380nm $\epsilon=8129$			
α -picoline	410nm $\epsilon=5319$			
Collidine	410nm $\epsilon=10211$			

while the 1:2 ratio is predominant in the other three systems (piperidine, quinoline and α -picoline, each with rubenic acid). The optimum concentration range for Pd with each reagent system is 3.0 to 8.4, 1.7 to 4.1, 1.87 to 4.3 and 1.87 to 4.3 ppm, respectively. Beer's law is obeyed in the range 1 to 8.4, 0.59 to 4.1, 0.625 to 4.375 and 0.625 to 4.375 ppm respectively. The corresponding Sandell sensitivities are 17, 13, 19 and 10.4 ng/cm². Copper(II), Co(II), Ni(II), Pt(IV), Mo(VI), V(V), W(VI), Mn(II) and Cr(III) interfere seriously.

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Di-2-pyridyl ketone phenylhydrazine	500 nm	13.4	Palladium(II) (0.5 to 4 ppm) is determined by complexation with the reagent (11 references).	134
Butyl xanthate	290nm $\epsilon=75000$	8.1	Palladium (6 to 180 nmol) is determined by extraction into benzene from aq. K butyl xanthate at pH 8.1 containing EDTA and the absorbance of the extract is measured. Extraction is quantitative if an excess of xanthate is present. Addition of 0.12M EDTA does not affect the extraction if the xanthate concentration is $>15 \mu\text{M}$. Beer's law is obeyed for extraction of the stated amounts of Pd into 15 ml of benzene solution, and the coefficient of variation is .12% at the 0.12 $\mu\text{mol level}$. Tl(I), Ag, Hg(II), Pt(II), Au(III), Ru(III), Os(VIII), $\text{S}_2\text{O}_4^{2-}$ and CN^- interfere seriously.	135

Name of the Reagent	λ_{max} , or working wavelength with ϵ	pH	Remarks	Refs
3-2-Thiazolylozo) pyridine-2, 6-diamine	655m $\epsilon=13700$	Acidic (HClO ₄)	The reagent reacts with Pd(II) in aq. HClO ₄ to give a blue 1:1 (Pd:R) complex and the absorbance is measured. Beer's law is obeyed for 0.6 to 4.5 ppm of Pd. The relative error is 0.7%. Bivalent Cu, Co, Fe, Ni, Zn, NO ₃ ⁻ , SO ₄ ²⁻ , and CO ₃ ²⁻ in 50- to 200-fold excess over Pd give no interference. Mercury(II), Au, Pt, Os, Ir, Ru, Rh, F ⁻ , Cl ⁻ , Br ⁻ , I ⁻ and SCN ⁻ interfere seriously. The method has been applied to 10 mg samples of four hydrogenation catalysts containing 4 to 10% of Pd.	136

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(2-Pyridylazo) resorcinol	610nm $\epsilon=3900$	4.5-5.0	To the sample (25 ml) containing 10 to 75 μg of Pd, 0.2 gm of Na salicylate is added. The pH is adjusted to 4.5 to 5.0 with dil. NaOH or HCl and the solution is shaken for 1 min. with mesityl oxide. A 2 ml portion of 0.1% reagent solution is added to the organic phase and the mixture is shaken for 90 sec. The organic phase is dried with anhydrous Na_2SO_4 and its absorbance is measured. Beer's law is obeyed in the range 10 to 75 μg . Sandell's sensitivity is 0.027 $\mu\text{g}/\text{cm}^2$. Copper, U, Th, EDTA and thiourea interfere seriously.	137
Sulphonitrophenol M [3-2-(hydroxy-5-nitro-3-sulphophenylazo)-6-(3-sulphophenylazo)chromotropic acid]	600nm $\epsilon=86000$	1mM-4M acid	Palladium sulphate forms a coloured complex with the reagent in an aq. medium 1mM to 4M in HNO_3 , H_3PO_4 , HClO_4 or H_2SO_4 .	138

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5-Diethylamino-2-(2-thiazolylazo) phenol(II)	625 nm	Acidic (H_2SO_4)	Sorption spectrophotometric determination of Pd in industrial objects has been reported. The Pd(II) is preconcentrated on Ku-2x8 cation exchange resin (particle size 0.1 to 0.25 mm) modified with 0.5 mmol/g of reagent (I) by stirring 10 g of resin (IIa) with 200 ml of 25 μM (II in 0.1M HCl) for 30 min. The test solution (10 to 200 ml), containing ≥ 20 ng/ml of Pd and 1.5M in H_2SO_4 is boiled with 0.3 g of the sorbent for 30 to 90 min. The sorbent with the retained Pd-(I) complex is separated and suspended in 1.5M H_2SO_4 , and the absorbance of the mixture is measured. Beer's law is obeyed for 0.02 to 1.5 $\mu g/ml$ of Pd. To enable amounts of foreign species relative to Pd are Cu, Ni, Co and Fe 20,000, Pt-group metals 50, and Cl ⁻ 1000. The method is used for determining 0.38 to 1.16% of Pd in industrial samples containing Cu, Ni, Co and Fe as major components and < 0.1% of other Pt-group metals. the coefficient of variation is < 6.8%.	133

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Chrome Azurol S [C.I. Mordant Blue 29]	610nm $\epsilon=30040$	6.0-6.2	The reagent forms a 2:1 (Pd:R) complex with Pd(II). The Pd-complex is formed in acetate buffer medium. For the determination of palladium with the reagent, the solution must be at pH $\approx$ 2 before the addition of reagent. The reagent also forms 2:1 (M:R) complexes both with Cu(II) and Be and a 1:1 complex is formed with Ti(IV), Zr, V(IV) and Fe(III). Optimum ranges λ max values and ϵ values of the complexes are: Cu - 6.4 to 6.8, 585 nm, 64,000; Be - 4.4 to 5.2, 570 nm, 59,200; Ti - 5.2 to 5.4, 565 nm, 26,700; Zr - 5.8 to 6.3, 600 nm, 15,100; V(IV) - 5.8 to 6, 535 nm, 27,300; and Fe - 5.4 to 6.2, 575 nm, 32,000. Complexes of Fe and Ti are formed in acetate medium, and the other complexes in hexamine buffer medium. The solution must be at pH $\approx$ 2 for Ti and Zr, 2 to 3.5 for Fe, V and Be, and 2 to 7 for Cu before the addition of reagent.	140

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
NN Dimethyl-N(4-methyl-5-nitro-2-thiazolyl) thiourea	413 nm	2.0	To a portion (0.5 ml) of a methanolic 1mM solution of the reagent, 10 ml of test solution is added (pH 2). After 5 min. the complex is extracted into 10 ml of CHCl_3 . The extract is washed with 10 ml of 1M NaOH , then the volume is adjusted to 10 ml with CHCl_3 . The absorbance is measured against CHCl_3 . Beer's law is obeyed for 3.3 to 22 μg of Pd in the extract. The chelates with Cu(II) , Ni(II) , Ir(IV) , Hg(II) and Au(III) are decomposed by the washing with NaOH solution.	141

Name of the Reagent:	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3,5-dibromo-2-pyridyl- azo-m-phenylenediamine	595 nm $\epsilon=73500$	5M H_2SO_4	The test solution (containing 5 to 40 μg of Pd) is allowed to react with 2 ml of ethanolic 0.05% reagent for 5 min, then 5 ml of 5M H_2SO_4 is added. The mixture is diluted to 25 ml with H_2O and the absorbance is measured. The colour is stable for 236h and is unaffected by acidity in the range 0.25 to 3M H_2SO_4 or 0.5 to 6M HCl or $HClO_4$. The reagent is more tolerant to foreign elements especially Ag, Cu(II), Ni, Co, Rh(III), Pt(IV) and Tl(I) as compared to other reagents.	142
5-Cl-PADAB 4-(5-Chloro-2-pyridyl- azo)-m-phenylenediamine	530nm 570nm $\epsilon=63000$	Acid/c	The reagent exhibits an absorption peak at 425 nm in 1M HCl medium. With addition of Pd and heating at 70° to 80° two further peaks at 530 and 570 nm appear. The positions of these two peaks remain unchanged on addition of reagent or Pd in excess, indicating formation of a 1:1 complex. Beer's law is obeyed for $\leq 32 \mu g$ of Pd	143

in 25 ml of solution. In the determination of 20 μg of Pd, there is no interference from 20 mg of Cr(VI); 1 mg of Mg, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb, Al, Cr(III), V(V), Pt(IV) or Zr; and 0.5 mg of Au(III).

2-Methyl-1,4-naphthoquinone: thiosemicarbazone	560nm $\epsilon=42000$	87	144
The solution containing 7.5 to 57.2 μg of Pd(II) is allowed to react for 1 h with a 30-fold excess of the reagent (as a 5mM solution in ethanol) in a medium of aq. 30 to 40% dimethylformamide buffered at pH 8.7 with alkaline acetate. The absorbance is measured against a reagent blank. Beer's law is obeyed for ≤ 2.66 ppm of Pd in the final solution. Ru, Rh, Ir and $\text{S}_2\text{O}_3^{2-}$ interfere.			

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Tin(II) and iodine	590nm	Acidic	Determination of palladium with tin (II) and iodide is reported. To a solution containing 5 to 120 μ g of Pd, 1.5 ml of 25% SnCl ₂ solution in 4M HCl, 12.5 ml of acetone and 6 ml of 80% KI solution are added. The mixture is diluted to 25 ml with H ₂ O and, after 20 min, the absorbance of the green complex is measured against a reagent blank. Serious interference is caused by Rh and Pt. The method has been used to determine Pd in 'white gold' alloy after dissolution of the sample by aqua regia.	145
3',5'-Dichloro-2'-hydroxyacetophenone oxime	400nm	2.0-4.5	A portion of Pd(II) solution is adjusted to pH 2 to 4.5, and a five-fold excess of a 0.05M solution of the reagent is added and set aside for 10 min. The mixture is then extracted with isobutyl methyl ketone (2 or 3x5 ml). The organic phase is diluted to 25 ml and the absorbance is measured. Bear's	146

law is obeyed for 11.1 to 89.0 ppm of Pd(II), and the reproducibility is $\pm 1.5\%$. Many foreign species do not interfere in > 4 -fold excess over Pd, but Cu(III) and V(V) interfere seriously.

147

Determination of palladium in wastes containing noble metals is reported. Noble metals are isolated, e.g. from slag from precious metal refining, by cupellation, and the button is digested with HNO_3 (1:1). The precipitated Ag is separated, the solution is treated with HCl (1:1) and AgCl is removed. To the resulting solution, containing $\leq 65 \mu\text{g}$ of Pd(II), 5 ml of acetate buffer solution (pH 5.0), 2 ml of 0.5mM reagent and 2 ml of 5mM Septonex cationic detergent are added. The mixture is made up to 25 ml with H_2O , and after 20 min., the absorbance is measured against a reagent blank. For Pd(II) contents of 0.2, 0.8 and 3.5%, coefficients of variation are 34.3, 1.2 and 9.5% respectively.

50

634 nm

Bromopyrogallol red

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(2-Pyridylazo) resorcinol	530nm	2.5	Determination of platinum (II) and palladium (II) with the reagent by reversed phase ion pair partition chromatography is reported. Pt(II) and Pd(II) each form a ternary complex with the reagent and Cl ⁻ after heating under reflux for 2 h in aq. 40% propan-2-ol at pH 2.5. The complexes are separated on a column of a Yanapak ODS-T with aq. 30% tetrahydrofuran containing 6.2 mM tetrabutyl ammonium bromide, 17mM NaCl, 0.27 mM EDTA and 16 mM acetate buffer (pH 5.6) as mobile phase. Detection limits are 1 μ M Pt(II) and 0.5 μ M Pd(II). Bivalent Ni, Cu or Co, Zn, Al, Cr(III) and Rh(III) do not interfere at concentration $\approx$ 0.1 mM. Fe(II) could be masked by 0.5 mM EDTA. The coefficients of variation ($n = 7$) are 1.70 and 1.52% for Pt(II) and Pd(II) respectively.	148

To determine Pd(II), the test solution is treated with 1 ml of 0.2% reagent (I) solution and 5 ml of NaOH-H₃BO₃ buffer solution of pH 9. The solution is diluted to 30 ml with H₂O, 1 ml of 0.025% cadion (II) solution is added, the complex is extracted with CHCl₃ and palladium in the extract is determined by spectrophotometry. Silver, Hg(II) Co, Cu(II), Cd and Ni have also been determined with the reagent. For Ag and Hg(II) the absorbance is measured at 525 and 470 nm respectively. To determine Co, Cu(II) and Cd, the test solution is made 0.3, 0.1 or 0.5M respectively in NaOH and treated with 1 ml each of (I) and (II) solution before extraction. The absorbance is measured at 498, 490 and 490nm respectively. To determine Ni, 4 drops of H₂SO₄ (1:3), 2 ml of 10% tartaric acid solution, 1 ml of (I) solution and 1 ml of (II) solution are added to a solution containing 2 µg of Ni, and 7 ml of 2M NaOH is added immediately. The mixture is diluted to 20 ml with H₂O before extraction with CHCl₃. The extract is set aside for 30 min., and the absorbance is measured at 505 nm.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	R. fs.
Chlorosulphonic acid [3,6-bis-(5-chloro-2-hydroxy-3-sulphophenyl)naphthalene, 2,7-disulphonic acid]	643 nm	Acidic (HClO ₄)	To a sample containing < 64 μ g of Pd(III), 10 ml of a 0.2 mM solution of the reagent, 1 ml of 2.5M NaClO ₄ are added. The mixture is diluted to = 20 ml and heated on a boiling water bath for 5 min. The solution is diluted and the absorbance is measured. A 3000-fold excess of Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ ; 1000-fold excess of F ⁻ , tartrate; and 200-fold excess of Pt(IV) do not interfere.	150
Pentane-2,4-bis-(o-mercaptophenyl) and [NN' pentane-2,4-diylidene bis (2-aminobenzene thiol)]	510 nm ϵ =5900	2.0	Palladium forms a 1:1 complex with the reagent at pH 2.0 Beer's law is obeyed for 2 to 16 ppm of Pd Sautell's sensitivity is 18 ng/cu. cm. Platinum (IV), Os (VIII), acetate and tartrate interfere.	151

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Pyridyl-2-thienyl (Z)-ketoxime	433 nm	6.0	Determination of trace amounts of palladium in a nickel-copper matte without preconcentration is described. The sample is digested with HCl and HNO ₃ , and the pH of the solution is adjusted to 4.5 before addition of an excess of EDTA to mask Ni, Fe and Cu. After re-adjustment of pH to 6.0 the solution is treated with the reagent, the complex with Pd is extracted into CHCl ₃ and its absorbance is measured. Beer's law is obeyed for 0.2 to 2 ppm of Pd in the CHCl ₃ extract. Results for a standard matte agree well with the true value.	152
NN-Dimethyl-N'-[5-nitro-4-(4-nitrophenyl)-2-thiazolyl]-thiourea	430nm	2.0	The reagent forms a 1:2 (Pd:R) chelate at pH 2.0. It is extracted into CHCl ₃ and the absorbance is measured. Beer's law is obeyed for up to 3 μ g/ml of Pd in the extract. The method has been applied to determination of Pd in palladized asbestos. Iron, Si, Al, Mg, Cu, Na and K in the asbestos do not interfere.	153

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	R ₂ fs.
Eriochrome Azurol B and hexadecyl trimethylammonium bromide	645 nm	5.5	The sample solution is mixed with the two reagents in buffer medium of pH 5.5. After 10 min, the absorbance is measured. Beer's law is obeyed in the range 0.2 to 1 $\mu\text{g/ml}$ of Pd(II).	154
8-Amino-5-phenylazoquinoline	620 nm $\epsilon=79000$	11.5-12.0	A green ppt. of the 2:1 (R:Pd) complex is formed on addition of excess of an ethanolic 0.12% solution of the reagent to a solution of Pd(II) at pH 3 (adjusted with formic acid and NaOH); followed by aq. NaOH to adjust the pH to 11.5 to 12.0. The complex is extracted into isobutyl methylketone. Beer's law is obeyed for $\approx 2.8 \mu\text{g/ml}$ of Pd(II) in the extract. Absorptive interference by metals precipitated at the extraction pH is eliminated by adding EDTA and interference from Pb and Zr is overcome by tartrate. Interference is caused by Au, Bi, Ru, Sb, I ⁻ , SCN ⁻ , CN ⁻ and S ²⁻ . Copper, Ir, Pt and Rh are tolerated in conc. similar to that of Pd. For 1.01 $\mu\text{g/ml}$ of Pd the coefficient of variation ($n=6$) is 0.8%.	155

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Bromopyrogallol red (I)	620nm	5.6	Palladium(II) is determined: i) at pH 5.6 (acetate buffer) by mixing the sample solution with (I) and, after 40 min, measuring the absorbance at 620 nm; ii) at pH 5.0 (acetate buffer) with (I) in the presence of (III) with measurement at 634 nm after 20 min; iii) at pH 6.0 (phosphate buffer) with (II) and measurement at 650 or 570 nm 120 min later, and iv) at pH 6.5 phosphate buffer (II) in the presence of (III) with measurement, after 20 min, at 700 nm. Between 0.41 $\mu\text{g/ml}$ and 2.66 to 3.72 $\mu\text{g/ml}$ of Pd(II) could be determined.	156
alone or in the presence of (1-ethoxycarbonyl) pentadecyl trimethyl ammonium bromide (II)	634 nm	5.0		
Catechol violet (II)	650 or 570nm	6.0		
alone or in the presence of (1-ethoxycarbonyl) pentadecyl trimethyl ammonium bromide	700nm	6.5		
Pyrogallol red and cetylpyridinium [hexadecylpyridinium] bromide	650nm $\epsilon=22500$	5.6	Palladium forms a ternary blue-green Pd-pyrogallol red hexadecylpyridinium bromide (1:1:3) complex at pH 5.6 (acetate buffer solution). Beer's law is obeyed in the range 0.1 to 8.5 ppm of Pd. Sandell's sensitivity is 1 ng/cm². Zirconium, VO(II), Ta and ClO₄⁻ interfere seriously.	157

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Blacetyl monoxime-2- pyridyl hydrazone	560nm	1.2-1.8	The sample solution (containing $\leq 100 \mu\text{g}$ of Pd is adjusted with HCl to pH 1.2 to 1.8. To it 0.5 ml of 1M KCl and 2.5 ml of an ethanolic 0.2% solution of the reagent are added. The complex is extracted by shaking the solution for 1 min with 10 ml of CHCl_3 . This extract is dried over Na_2SO_4 and its absorbance is measured against H_2O . The colour remains stable for several days if the solution is kept at a low temperature. Beer's law is obeyed between 1.93 to 12.06 ppm of Pd in the organic extract. At ≤ 1.93 ppm the results are less precise. There is little interference from other elements if the pH is adjusted before the reagent is added and a sufficient excess of the reagent is used. Determination of Pd in a Pd- CaCO_3 catalyst has also been described.	158

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Picolinaldehyde amidinohydrazone	440nm	4.5	The reagent forms two yellow complexes of stoichiometry 1:1 and 1:2 (R ₂ Pd) with Pd (II). The test solution containing $\leq 655 \mu\text{g of Pd}$ is treated with acetate buffer solution of pH 4.5 and a solution of the reagent, and the absorbance is measured.	159
Iodide and pyronine G	575nm $\epsilon=95800$	3.5	To a mixture of 2.5 ml each of a 1.10% KI, a 1.0021% pyronine G, and 20% citrate buffer solution (pH 3.5), 1 ml each of a 1.10% ascorbic acid and 1% gelatin solution are added with stirring. To it a portion of PdCl ₂ solution in dil. HCl is added. The solution is diluted to 25 ml and its absorbance is measured against a reagent blank. Os(VIII), Ru(III) and Ir(IV) do not interfere. Bi(III) is masked with oxalic acid, but Pt interferes at all levels and prior separation is required.	160

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thiodibenzoylmethane	465 nm	3.0-5.0	Separation and determination of palladium by synergic extraction is reported. An aqueous solution of pH 3 to 5, containing 0.5 to 8 $\mu\text{g/ml}$ of Pd(II) is shaken for 10 min. with an equal volume of 0.05M reagent in ethyl methyl ketone. The organic phase is separated and its absorbance is measured against a reagent blank. Beer's law is obeyed for 0.5 to 8 $\mu\text{g/ml}$ of Pd.	161
Ammonium thiocyanate with either of the following			Determination of palladium using mixed ligand complex formation with pyridine, α -picoline, β -picoline, γ -picoline or 2,4,6-collidine and thiocyanate has been discussed. The test solution containing 10 to 100 μg of Pd(II), is mixed with 1.5 ml of aq. 2% NH_4SCN and 1 ml of pyridine or either α - or β - or γ -picoline or 2,4,6-collidine and the mixture is adjusted to pH 4.9 to 7.1, 3.5 to 7.0, 2.6 to 5.8, 4.9 to 6.6 or 1.2 to 2.1, respectively, with 0.1M HCl or	162
i) Pyridine	315 nm $\epsilon=13900$	4.9-7.1		
ii) α -p'coline	304 nm $\epsilon=25100$	3.5-7.0		
iii) β -p'coline	306 nm $\epsilon=25100$	2.6-5.8		
iv) γ -p'coline	305 nm $\epsilon=21300$	4.9-6.6		

NaOH. The resulting solution is diluted to 20ml with H₂O and extracted with 20 ml of CHCl₃, and the absorbance of the extract is measured at the corresponding wave length. Sandell's sensitivities for the five Pd complexes are 7.76, 4.2, 5.1, 5.0 and 5.5 ng/cm² respectively. Beer's law is obeyed in the ranges 0.8-7.7, 0.4-4.52, 0.5-5.5, 0.5-5.0 and 0.5-5.5 µg of Pd(II)/ml for pyridine, α-picoline, β-picoline, γ-picoline and 2,4,6-collidine systems respectively. Mercury(II), Fe(III), Co(II) and Cu(II) interfere in every system.

1.2-2.1

310nm
ε=32100

v) 2,4,6-collidine

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Mercaptoacetanilide	518nm $\epsilon=7570$	0.3-1.0	A 1:2 (Pd:R) complex is formed between the reagent and Pd in a medium of pH 0.3 to 1.0. The complex is extracted into CHCl_3 and the absorbance of the extract is measured. The recommended working range is 0.1 to 11.0 ppm for Pd. Sandell's sensitivity is 14 ng/cm ² . There is no interference from associated noble or base metals. Platinum has also been determined with this reagent and forms a 1:2 (Pt:R) complex in a medium of 2 to 4M in HCl. The complex is extracted into CHCl_3 and the absorbance is measured at 593nm. The working range is 0.2 to 16.0 ppm for Pt. The Sandell sensitivity and ϵ values are 19 ng/cm ² and 9560 respectively.	193

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
p-Anisaldehyde thiosemicarbazone	370nm $\epsilon=21600$	2.9-4.3	The reagent instantaneously forms a 1:1 yellow complex with Pd(II) at room temperature. Beer's law is obeyed over the range 0.06 to 3.3 ppm for Pd. Sandell's sensitivity is 4.9 ng/cm ² . The reagent also forms a 1:2 (Cu:R) orange-yellow complex with Cu(II) (0.1 to 0.75M NaOH), which has λ max at 402 nm. Beer's law is obeyed over the range 0.1 to 10 ppm for Cu. The ϵ value and Sandell's sensitivity are 6100 and 10.4 ng/cm ² respectively.	164
1,3-Cyclohexanedione bithiosemicarbazone monohydrochloride	360nm $\epsilon=11000$	1.5-3.5	The reagent forms a 1:1 stable brown yellow complex with Pd(II). Beer's law is obeyed for 0.5 to 4.5 ppm of Pd with an optimum concn. range of 1.0 to 4.0 ppm of Pd as evaluated by Ringbom's method. Sandell's sensitivity is 9.67 ng/cm ² .	165

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-Nitrosodimethyl-aniline	525nm	2.2	Traces of palladium are determined in sulphuric acid filtrates. The sample is evaporated with aqua regia (to remove Na_2S) and then with HCl before co-pptn. of the Pd (1 to 15 μg) with Te from 2.5M HCl medium by addition of SnCl_2 solution. A solution of the ppt in aqua regia is evaporated, the residue is heated to dryness with HCl-KCl and then with HCl . The aq. solution of the final residue is adjusted to pH 2.2 (Na-acetate- HCl buffer), treated with the reagent solution, diluted with ethanol and the absorbance is measured. The standard deviation is $\pm 0.1 \mu\text{g}$ for a range of samples containing 32 to 488 $\mu\text{g}/\text{l}$ of Pd.	166

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Eriochrome cyanine R [C.I. Mordant Blue 3] (I)	575nm $\epsilon=46000$	≈ 6.4	Palladium(II) forms a coloured 1:2 (Pd:R) complex with the dye at pH ≈ 6.4 . The pH is adjusted with an acetate buffer solution and the pH of the test solution before the addition of dye and the buffer should be ≈ 2 . Copper(II), Be, V(IV) and Fe(III) also form coloured complexes with the dye. The metal-ligand ratio, optimum pH, λ max and ϵ values of the complexes are: Cu - 1:1, pH ≈ 6.4 , 535 nm and 22,000; Be - 1:1, pH ≈ 6.7 , 525 nm and 36,000; V(IV) - 1:2, pH ≈ 6.1 , 545 nm and 46,000; Fe(III) - 1:2, pH ≈ 6.3 , 560 nm and 47,000. The pH is adjusted with a hexamine buffer solution for the V(IV) - (I) complex or with an acetate buffer solution for the other complexes.	167

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Ref's.
Semi-methylxylenol blue	569nm	Acidic (HNO ₃)	The sample solution containing 10 to 80 μg of Pd is acidified with 1 M HNO ₃ and 3 ml of a 0.05% solution of the reagent is added. The solution is diluted to 20 ml with H ₂ O and heated for 5 min. in a boiling water bath. It is cooled and diluted to 25 ml, and the absorbance is measured. Beer's law is obeyed for 0.4 to 3.2 μg ml of Pd. Bismuth (III) has also been determined with this reagent. The sample solution containing 10 to 100 μg of Bi (III) is acidified with 1M HNO ₃ and 3 ml of 0.05% solution of reagent is added. The solution is diluted to 25 ml and the absorbance is measured at 568 nm. Beer's law is obeyed for 0.4 to 4 μg /ml of Bi(III).	168

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Propioniclazine {2-Cyano-10-[3-(4-hydroxy-1-piperidyl)propyl] phenothiazine}	474 nm $\epsilon = 4100$	1.10-4.10	To a portion of sample solution containing 5 to 605 μg of Pd(II), 5 ml of Na acetate HCl buffer (pH 2.65) and 3 ml of a 10% reagent are added. The solution is diluted to 25 ml with H_2O and shaken, and the absorbance is measured. The complex has 1:1 (Pd:R) stoichiometry. Beer's law is obeyed for 0.2 to 24.2 ppm of Pd(II) in the final solution. Determination of 2 to 10 ppm of Pd(II) showed a max. relative error of $\pm 1.2\%$ and a max. standard deviation of 0.016 ppm. Thiouphane, EDTA, Ag, Au, IO $^-$, MnO $^{2+}$, Cr $^{3+}$ and VO $^{2+}$ interfere. The method has been applied to the determination of Pd in jewelry alloys.	169

Name of the Reagent:	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-Amino-5-nitrosopyrimidine-2, 6-diol	400nm $\epsilon=18800$	Acidic	The reagent forms a brown yellow 1:2 (Pd:R) complex with Pd(II). To the test solution containing 18 to 150 μg of Pd, 2 ml of the reagent are added and the absorbance is measured. Beer's law is obeyed for up to 10 ppm of Pd. Sandell's sensitivity is 0.005 $\mu\text{g}/\text{cm}^2$. Thiourea interferes seriously. The coefficient of variation ($n=6$) is 0.33% for a standard solution containing 2.7 ppm of Pd. The reagent has been used for the determination of Pd in alloys and minerals.	170
Thiopyrogallol (I) and β -Mercaptosorcylic [4-hydroxy-2-mercaptobenzoic] acid (II)	430nm $\epsilon=9600$ 430nm $\epsilon=11000$	5.0 5.0	Both the reagents (I) and (II) form a 1:2 (Pd:R) complex with Pd at pH 5 in aq. 60% ethanol. Beer's law is obeyed for 0.5 to 6 ppm of Pd with reagent (I) and (II). Sandell's sensitivities are 0.01 and 0.010 $\mu\text{g}/\text{cm}^2$ of Pd respectively for (I) and (II). Up to 200 ppm of Cd, Zn, Mg, Ca, Al, or Pt(II) and 400 ppm of citrate, tartrate, oxalate, NO_3^- , F^- , SO_4^{2-} ,	171

PO_4^{3-} , EDTA or SCN^- do not interfere. Nickel, Co, WO_4^{2-} , MoO_4^{2-} , VO_3^- , Ru(III), Ir(IV) and Rh(III) interfere.

Imipramine (10 hydrochloride 490 nm Acidic

Determination of palladium(II) as imipramine tetraiodopalladate is reported. Imipramine (I) hydrochloride reacts with halo-complexes of Pd(II) in acid medium to form 2:1 (I)-Pd complexes that are insoluble in H_2O . The $(\text{H(I)})_2\text{PdI}_4$ is readily soluble in CHCl_3 . This reagent has been used in the determination of Pd (0.5 to 15 $\mu\text{g/ml}$) in solution. Tenfold amounts of Sn(II), Mg , Ca, Ni, Mn(II), As(III), Cr(III), Ba, Cl^- , NO_3^- , acetate, PO_4^{3-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- and CO_3^{2-} do not interfere. A five-fold excess of Ag, Pt(IV), Cu(II), Cd or Co(II) increases the result by 2.5%. For an imina based catalyst containing 8.76% of Pd, the error is 0.51% ($n=5$).

Name of the Reagent	λ_{max} , or wavelength with ϵ	pH	Remarks	Refs.
1-(2-Amino-p-tolyl)-4,4,6-trimethyl-1H,4H-pyrimidine-2-thiol	440nm	Acidic	Palladium in aq. solution forms a yellow complex with methanolic reagent in the presence of HCl and the absorbance is measured. The method is suitable for solution containing 43 to 190 μ g of Pd in a final volume of 10 ml with a methanol content of 50%.	172
Thio-Michler's ketone	530nm $\epsilon=190000$		The sample is mixed with dimethylformamide solution of the reagent and hydroxyl-ammonium chloride. After 10 min., the absorbance of the complex is measured. Beer's law is obeyed for 0.1 to 0.5 ppm of Pd(II). The coefficient of variation is 1% for 10 determinations of 0.3 ppm of Pd. The method has been used to determine trace amounts of Pd in antibiotics and in catalysts for car-exhaust purifiers.	174
5-(3,5-Dibromo-2-pyridylazo) toluene-2,4-diamine	600nm $\epsilon=105000$	Acidic (HCl)	Determination of palladium in ores with the reagent after concentration by extraction in the presence of zephiramine [benzyl-dimethyl tetradecyl ammonium chloride] has been described. In the basic method, (without extraction) the test	175

solution is treated with 1 ml each of HCl (1:2) and ethanolic 0.03% reagent. It is diluted to 10 ml with H₂O and heated at 70° to 80°, for 5 min. The cooled solution is treated with 12 ml of ethanolic HCl and diluted to 25 ml with 0.4M HCl and the absorbance is measured against a reagent blank. Beer's law is obeyed for 0.5 to 10 µg of Pd. To determine Pd in ores, the sample (0.5 to 20 g) is roasted for 1 h at 700°, and the residue is heated with 50 ml of HCl, with addition of aq. H₂O₂ (2x10 ml), followed by boiling for 30 min. and evaporation to ~10 ml. The residue is boiled with 20 to 40 ml of H₂O, and the hot solution is filtered, and the filter is washed with hot 1% HCl and then with hot H₂O. A suitably diluted portion of the filtrate is shaken with 10 ml each of aq. 2.5% zephiramine and 1,2-dichloroethane. The organic phase is shaken with 2 ml of 0.2M HCl and the separated organic phase is treated with 3 drops of 20% NaCl solution and evaporated to dryness on a boiling water bath. The residue is dissolved in 0.4M HCl and treated with 1 ml of the ethanolic reagent for further treatment according to the basic method.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3-Acetoxy-7-methylphenothiazine	540 nm 550 nm $\epsilon=7400$	2.5-3.0	The reagent forms a blue violet 1:1 complex with Pd(II) that is suitable for determination of 1.7 to 2.9 ppm of Pd at pH 2.5 to 3.0. Sandell's sensitivity is 15 ng/cm ² . Tolerance limits (μ g) for other species are: Ru(III) 4; Rh(III) 12; Fe(III) 3; Os(VIII) 0.7; Pt(IV) 0.6; Ir(III) 14; Co(II) 125; Ni(II) 25; Cu(II) 2; NO ₃ ⁻ 200; SO ₄ ²⁻ 200; Cl ⁻ 300 and Br ⁻ 270.	176
4-(3,5-Dichloro-2-pyridylazo)-m-phenylenediamine	588 nm $\epsilon=82000$	1M H ₂ SO ₄	Palladium reacts with the reagent in acidic ethanolic medium to form a violet blue complex with λ max at 548 and 588 nm. In 1M H ₂ SO ₄ and 8% of ethanol, Beer's law is obeyed for <2.5 ppm of Pd. The optimum range is 0.2 to 1.4 ppm	177
Pseudopurpurin	670 nm $\epsilon=77000$		A solution containing 7.5 to 60 μ g of Pd (II) is mixed with 5 ml of ethanolic 0.25 mM pseudopurpurin. After 10 minutes, 2 ml of 5M ethanolic ammonia is added and the mixture is made up to 25ml with ethanol. The absorbance of the green blue complex is mea-	178

sured against 80% ethanol. Beer's law is obeyed for 0.30 to 2.40 ppm of Pd(II). The standard deviation is 0.0172. There is no interference from a 100-fold concn of Ni(II) or a 10-fold concn. of Pb(II) relative to Pd.	179
Palladium (II) forms a yellow complex with a fourfold excess of reagent in an aq. 50% alcoholic medium of pH 1.2 to 3.8 and the absorbance is measured. Determination of 0.16 to 12.9 $\mu\text{g/ml}$ of Pd(II) has been reported.	1.2 3 8
385 nm	3-(2-Furyl)-2-imercapto propionic acid
180	To determine Pd(II) the test solution [final Pd(II) concn. of 0.04 to 0.24 mM] is treated with aq. methanolic 1mM bromazepam and buffer solution of pH 5.0 and made up to the volume with H_2O . The absorbance is measured after 30 min. Flurazepam under similar conditions of pH etc. has also been used for determining 0.02 to 1.8 mM Pd(II). In this case absorbance is measured after 1h of mixing the solutions.
5.0	288 nm
5.0	$\epsilon=8300$
331 nm	Bromazepam and Flurazepam
$\epsilon=7400$	

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
9-(2-(2,2'-bipyridyl)azo)-phenanthrene-10-ol	647 nm	2.0	The solution containing 40 μg of Pd is treated with trichloroacetic acid-trichloroacetate buffer of pH 2.0 and ethanol to give a final concn. of 50% (V/V). The solution is diluted with buffer and the absorbance is measured. Alternatively, the complex is extracted into CHCl_3 , and after drying the extract with Na_2SO_4 , absorbance is measured at 657 nm for Pd. Nickel and copper have also been determined separately with this reagent. To a solution containing < 8 μg of Ni and 15 μg of Cu, acetic acid-Na acetate buffer of pH 4.5 are added, and also ethanol to give a final concn. of 50% (V/V). The solution is diluted with buffer solution and the absorbance is measured at 552 nm for both Ni and Cu. Alternatively, with the ethanol concentration adjusted to 20% and warming to 70° in the determination of Ni, the complexes are extracted into CHCl_3 , and after drying the extracts with Na_2SO_4 the absorbance is measured at 555 nm for Ni and 560 nm for Cu.	181

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Bis-(2-ethylhexyl) hydrogen phosphoro-dithioate	295 nm $\epsilon=31,000$	NH ₄ Cl-NH ₄ OH buffer	Microgram amounts of Pd(II) are separated from amounts of Ca, Sr, Ba, lanthanoids, Al, Mn(II), Fe(III), Zn, Cd, Tl(I), Sn(II), Sn(IV), Pb, Co, Ni, Bi, Sb, As(III) and Cu by extracting the Pd with 1 mM reagent in toluene from aq. solution containing 0.1 to 10M NH ₃ and 0.1 to 5.3M NH ₄ Cl. Pd can be determined directly in the extract by measuring the absorbance of the 1:2 (Pd:R) complex. Tolerable amounts of diverse metals relative to Pd are: Ca, La, Ni or Cd 600; Al, Zn, Sn, Mo(IV), Fe(III) or Sb 500; Au or Pt 5; Ag 20; Cu(II) (100); Mn(II) (400); Pb(500) and Co(200) must be masked with EDTA. The method has been used for determining 0.23 μ g/ml of Pd in spent palladium-plating electrolytes containing also 40 mg/ml of NH ₄ Cl, 32 mg/ml of NH ₃ , 0.15 mg/ml of maleic anhydride, 0.28 mg/ml of Cu and 0.11 mg/ml of Ni. The coefficient of variation is <3%.	182

Name of the Reagent	λ_{max} , or working wavelength with ϵ	pH	Remarks	R:fs.
1,3-Bis(cis-4-mercapto-5-phenylthiourea	410 nm	2M HCl	The test solution, 10 to 30 ml, is made 2M in HCl and Pd is extracted with 5mM reagent in dichloroethane and absorbance of the extract is measured. Beer's law is obeyed for 1 to 20 $\mu\text{g/ml}$ of Pd. Palladium has also been determined from a mixture of Pd, Pt, Rh and Ir using this reagent. Details have also been given on determination of Pt, Rh and Ir with the help of this and other similar reagents. Amounts of diverse metals that could be tolerated are Ni and Pb 20,000; Co 10,000; Fe 3800 and Cu 500. The method is used for determining ≈ 30 to 60 ppm of Pd in technological products.	183
Nitroxaminazo [4-amino-3-(2-hydroxy-5-nitro-3-sulphophenyl) azo] naphthalene-2,7-disulphonic acid]	570 nm 640 nm	1.5M H_2SO_4	Microgram amounts of Pd(II) are concentrated on AV 17x8 anion exchanger (modified with 2.5 μg mol/g of nitroxaminazo) by heating 10 ml of test solution (1.5M in H_2SO_4) containing 2 to 16 μg of Pd with 0.4 g of the modified exchanger at 90° for 30 min. The absorbance of the concentrate with the retained Pd(II) nitrox-	184

aminazo (1:1) complex is measured at 570nm or 640nm. Tolerable amounts of diverse ions relative to Pd are Cu, Zn, Fe(III), Ni, Co and Cr(III) (10,000) and platinum group metals (1). The method is used for determining ≈ 1 ppm to 0.6% of Pd in metallurgical samples containing 20% of Fe, 2% of Ni and 0.5% of Cu and in technological solutions containing ≈ 65 to 150 mg/l of Ni, Cu, Fe and Co. The coefficient of variation is $< 12.6\%$ ($n=6$).

Dithizone	635 nm	Acidic	185
Extractive separation and spectrophotometric determination of palladium and platinum with dithizone in the presence of stannous chloride is reported. Palladium is first extracted with 0.2mM dithizone in CCl_4 from a medium 1M in H_2SO_4 and 0.1M in HCl, then aq. $SnCl_2$ and HCl are added to the aq. phase for reduction and Pt is extracted with dithizone into $CHCl_3$. The absorbance of the extracts is measured at 635 and 710 nm for Pd and Pt, respectively. Gold, Hg, and Cu do not interfere.			

Name of the Reagent	λ_{max} , or working wavelength with ϵ	pH	Remarks	Refs.
Benzyl dimethyl phenylammonium [benzyl dimethyl anil- inium] chloride	450 nm $\epsilon=5340$	3.4-5.8	The test solution, containing 5 to 160 μg of Pd, is diluted to 5 ml with H_2O . The pH is adjusted to 3.4 to 5.8 with aq. acetate buffer and 1 ml each of aq. 5% KI and aq. 0.24% reagent are added. The mixture is extracted for 2 min. with 5 ml of 1,2-dichloroethane, and the absorbance of the extract is measured against the solvent. Beer's law is obeyed for 1 to 32 $\mu\text{g}/\text{ml}$ of Pd. Sandell's sensitivity is 20 ng/cm^2 . In the determination of 50 μg of Pd, interference - from Cu and Bi is prevented by masking with EDTA, from Fe(III) and Mo by masking with NH_4F , and from MnO_2 by reduction with oxalic acid before addition of the KI. Equal amounts of Pt and $\text{S}_2\text{O}_3^{2-}$ interfere seriously.	186

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Tetramethylthiuram monosulphide	345 nm	3.5	The solution containing Pd is mixed with 23.5 mM reagent in toluene. After 2 min. the organic layer is removed and the absorbance is measured. Beer's law is obeyed for 0.5 to 7.0 ppm of Pd. Palladium was determined by this method in a synthetic solution corresponding to brazing alloys and resistors. Osmium has also been determined with the reagent. The osmium solution is diluted with 2M HClO ₄ before the addition of 0.2% reagent in acetone. The mixture is heated, cooled and then extracted with CHCl ₃ and the absorbance of CHCl ₃ layer is measured at 580 nm. Beer's law is obeyed for 5 to 45 ppm of Os.	187
i) Thiocaprolactam ii) Pyrrolidine-2-thione iii) Piperidine-2-thione with Rose Bengal (C.I. Acid Red 94)	570 nm	6.0	Palladium (II) forms a complex with each of the thiolactam and Rose Bengal in an aq. medium pH 6.0. The complex is extracted into CHCl ₃ and the absorbance is measured. Beer's law is obeyed for 0.1 to 2.5 $\mu\text{g/ml}$ of Pd. Interference from Pt(IV) is observed.	188

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thioridazine hydrochloride	500 nm $\epsilon=3970$	2M H_3PO_4	The reagent forms a pink coloured complex with Pd. The sample solution is mixed with 5 ml of 10M H_3PO_4 and 5 ml of aq. 0.2% reagent, then diluted to 25 ml and the absorbance is measured. Beer's law is obeyed for 0.3 to 24.0 ppm of Pd. Sandell's sensitivity is 24 ng/cm ² . Interference is shown by Ag(I), Au(III), Os(VIII), Pt(IV), I ⁻ and EDTA. Ruthenium(III) has also been determined with the reagent and forms a blue radical cation. The absorbance of the complex is measured at 640 nm ($\epsilon=4970$). Beer's law is obeyed for 0.2 to 14.0 ppm of Ru. Sandell's sensitivity is 20 ng/cm ² .	189
2-Hydroxy-1-acetonaphthone oxime	376 nm $\epsilon=13000$	6.2	Palladium (II) forms 1:2 (Pd:R) yellow complex with the reagent in ethanol. A portion of 0.01M $PdCl_2$ solution containing 10 to 65 μg of Pd is mixed with 1 ml of 0.02M reagent in ethanol. The pH is adjusted to 6.2 with aq. 0.5M Na acetate. The complex is extracted with 10 ml of $CHCl_3$ by shaking for 2 min, and the	190

absorbance is measured against a reagent blank. Beer's law is obeyed for 10 to 65 μg of Pd in 10 ml of CHCl_3 . Sandell's sensitivity is 8.2 ng/cm^2 . Cerium(III), Fe(II), U(VI), Zr(IV), F^- , SCN^- and EDTA interfere.

191

5.6

378-
380 nm
 $\epsilon=9300$

1-Hydroxy-2-aceto-
naphthone oxime
(1-HANO)

Palladium (III) forms a 1:2 (Pd:R) dark yellow complex with the reagent. The complex is extracted in CHCl_3 . Beer's law is obeyed for 1.0 to 5.5 $\mu\text{g}/\text{ml}$ of Pd. Sandell's sensitivity is 0.011 $\mu\text{g}/\text{cm}^2$. In a binary mixture Pd is extracted first at pH 5.6 and the pH is then raised for extraction of the second metal. Co (II) and Ni (II) have also been determined with the reagent. Cobalt forms a 1:2 (Co:R) brown complex and nickel forms a 1:2 (Ni:R) greenish yellow complex. The λ_{max} and selected pH are 380 nm ($\epsilon=5650$) and 8.6 for cobalt and 396 nm ($\epsilon=5750$) and 9.0 for Ni. Beer's law is obeyed for 2.0 to 7.0 and 1.0 to 6.5 $\mu\text{g}/\text{ml}$ of Co and Ni respectively. Sandell's sensitivities are 0.010 $\mu\text{g}/\text{cm}^2$ and 0.010 $\mu\text{g}/\text{cm}^2$ for Co and Ni respectively.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3', 5'-Dibromo-2',4'-dihydroxyacetophenone oxime	360 nm $\epsilon=8250$	2.5-8.5	The reagent forms a 1:2 (Pd:R) complex with palladium (II) which is extracted into tributyl phosphate from 25% ethanolic medium at pH 2.5 to 8.5. Beer's law is obeyed for 1.0 to 10 ppm of Pd. Sandell's sensitivity is 12.8 ng/cm ² . Common anions, alkali and alkaline earth metals, NH ₄ , Be and Cd are tolerable in all determinations in 5 to 50-fold excess. Up to 10-fold excess of Mg, Co or Ag is also tolerated. Copper(II) and nickel(II) have also been determined with the reagent and also form a 1:2 (M:R) complex with the reagent. The λ_{max} and ϵ values are 3340 nm and 9000 for Cu(II) and 360 nm and 11200 for Ni(II). Both complexes are extracted into tributyl phosphate from 25% ethanolic medium at pH 3 to 9 and 5 to 8 respectively. Beer's law range and Sandell's sensitivities are 0.3 to 6.5 ppm and 7.1 ng/cm ² for copper and 0.3 to 6.0 ppm and 5.2 ng/cm ² for nickel.	192

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Promazine hydrochloride	498 nm $\epsilon=9610$	4.5-5.5	Palladium(III) forms a red 1:1 (Pd:R) complex with the reagent at pH 4.5 to 5.5. Beer's law is obeyed for 0.2 to 9.5 ppm of Pd(II). Sandell's sensitivity is 11 ng/cm ² . The method has been applied to the determination of Pd in a jewellery alloy and stibipalladinite mineral. Both Os (VIII) and Os(VI) also form a red radical cation in 1 to 3M HCl which has λ max at 515 nm. the molar absorptivity is 24000 for Os (VIII) and 18000 for Os(VI). Sandell's sensitivities are 7 ng/cm ² for Os(VIII) and 9.2 ng/cm ² for Os(VI). Beer's law is obeyed for 0.25 to 7.5 ppm of Os(VIII) or 0.25 to 8.0 ppm of Os(VI).	193

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
N-(Methoxyphenyl)-2-thiopicolinamide (I)	440 nm	1.6-3.2 M HCl	Palladium forms coloured complexed with the methoxy derivative in 1.6 to 3.2 M HCl and with the methyl derivative in 2.4 to 4.0M HCl. The complexes are extracted into CHCl_3 and the absorbances of the extracts are measured. Beer's law is obeyed for 1 to 6 and 1 to 8 ppm of Pd with reagent (I) and (III), respectively, the relative error for both reagents in these ranges being 2.7%. There is serious interference from Mo, V, W, Os(VI) and SCN^- .	194
N-p-Tolyl-2-thiopicolinamide (II)	440 nm	2.4-4.0 M HCl		
Allylthiourea	292 nm $\epsilon=22900$	Strongly acidic	Beer's law is observed for up to 12 $\mu\text{g/ml}$ of Pd in strongly acidic medium. The detecton limit is 0.14 $\mu\text{g/ml}$. The reagent has been claimed to be more sensitive and selective than 2-thiobarbituric acid.	195

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4,4',4"-Nitriloytris-[4'-diethylamino]azo benzene [Pallatriazo]	570 nm	Acidic	The acidic solution of sample reacts with the reagent in dimethylformamide medium, with heating, and the absorbance is measured after cooling. The reagent has been used for determination of 0.05 to 4 $\mu\text{g/ml}$ of Pd(II) in the presence of a 30-fold excess of Pt(IV).	196
Phenanthrene-9,10-quinone monoxime	430 nm $\epsilon=21200$	1.9-5.5	When 1ml of ethanolic 1mM reagent is added to ≈ 30 ml of an aq. solution containing 3 to 35 μg of Pd at pH 1.9 to 5.5, complex formation occurs. The complex is coprecipitated by addition of 2.0% naphthalene solution in acetone the ppt. is dried and dissolved in CHCl_3 , and the absorbance of the solution is measured. Interference from Fe (III), Co(II), Ni(II) and Cu(II) is prevented by addition of 4 ml of 2mM EDTA to the sample solution.	197

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Thiobarbituric acid	374 nm $\epsilon=10000$ 386 nm $\epsilon=7500$		Palladium(II) forms 2:3 and 1:3 complexes the reagent in aq. and in aq. 30% ethanolic medium respectively; the corresponding λ max are 374 and 386 nm. Beer's law is obeyed for up to 10 and 6 $\mu\text{g/ml}$ of Pd, respectively. The detection limits are 0.13 $\mu\text{g/ml}$ in aq. medium and 0.18 $\mu\text{g/ml}$ in aq. ethanol. Sandell's sensitivities are 0.0106 and 0.0141 $\mu\text{g/cm}^2$ respectively.	198
2,2'-Bipyridyl 2-pyridyl hydrazone (DPPH) [Dl-(2-pyridyl) ketone 2-pyridylhydrazone]	585 nm $\epsilon=19000$	2-10	Palladium(II) forms a red 1:1 complex with the reagent. A mixture of a solution of Pd(II) and an ethanolic 0.02M slution of DPPH is made 0.5 to 1.5M in HCl and extracted for 10 min. with CHCl_3 . A 5:1 ratio of the complexing reagent to Pd(II) is required. Extraction of Pd(II) in the pH range 2 to 10 is almost complete. Beer's law is obeyed in the range 0.5 to 1.5 ppm. The method is used to determine Pd in dental alloys.	199

Phenanthraquinone mono imine	430 nm $\epsilon=20720$	2.0-5.4	Palladium reacts with the reagent to form a water soluble, coloured, thermally stable complex that can be extracted into molten naphthalene in the pH range 2.0 to 5.4. The naphthalene phase is dissolved in CHCl_3 and the absorbance of this solution is measured against a reagent blank. Beer's law is obeyed for 4.0 to 37.0 μg of Pd in 10 ml of CHCl_3 . Sandell's sensitivity is 5.1 ng/cm^2 . Iron(III), Co(II), Ni(II), Cu(II) and Ir(III) when present in 1 mg amounts interfere. Such interference could be masked by 5 ml of $2 \times 10^{-3}\text{M}$ solution of EDTA before extraction.	200
Sulphonitrazo E [8-hydroxy-7-(2-hydroxy-5-nitro-3-sulphophenylazo) naphthalene-1,6-disulphonic acid]	555 nm	Acidic	The test solution is mixed with 10 ml of $20\text{M H}_2\text{SO}_4$, 1 ml of 85% H_3PO_4 and 10 ml of the reagent (0.2%). The mixture is heated at 65° for 30 min, cooled, and the absorbance is measured. The procedure is suitable for determination of 0.2 to 0.9 mg of Pd. Large amounts of other precious metals and non-ferrous metals do not interfere.	201

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Bis-(2-ethylhexyl) phosphorodithioate	540 nm	NH_4OH NH_4Cl	To a portion of the sample are added a few drops of 30% H_2O_2 . It is boiled, cooled and mixed with 2.5 ml of aq. 25% NH_3 . 25 ml of 0.1M EDTA and 25 ml of 2M NH_4Cl . Palladium is extracted from this solution into 10 ml of 0.01M reagent in heptane, and the absorbance of the extract is measured. Beer's law is obeyed for $<100 \mu\text{g/ml}$ of Pd. Large amounts of alkali and alkaline earth metals, lanthanoids, Al, Mn, Fe, Zn, Cd, Tl, Sn, Pb, Co, Ni, Bi, Sb and As do not interfere. Copper has also been determined with this reagent. The sample (second portion) is acidified with 10 ml of 3M HCl and copper is extracted into 10 ml of 0.025 M reagent in heptane. The absorbance of the extract is measured at 420 nm. Beer's law is obeyed for $< 5 \mu\text{g/ml}$ of copper.	202
5-Methyl-2-furaldehyde-2-benzothiazolyhydrazide zone	425 nm $\epsilon=29000$	0.6-2.8	Divalent Pd forms a stable 1:2 (Pd:R) complex with the reagent which is extracted from acidic medium into benzene and the absorbance is measured. Beer's law	203

is observed for 0.4 to 3.5 $\mu\text{g/ml}$ of Pd. The procedure has been applied to dental alloys containing 2 or 5% of Pd.	The reagent forms a blue 1:1 complex in strongly acidic solution. Beer's law is obeyed for up to 20 g of Pd(II) in 5 ml of final solution.	204
2-(5-Bromo-2-pyridyl azo)-5-diethylamino phenol	590 nm $\epsilon=43000$	Strongly acidic
NN'-Didecylidithio-oxamide	445 nm 538.5 nm	Simultaneous determination of platinum and palladium in minerals and rocks is reported. The digested sample is shaken for 1 min. with light-petroleum- CHCl_3 (3:1). 0.2% reagent in acetone in 1 aq. 50% SnCl_2 (20:4:1). The absorbance of the organic phase is then measured at 445, 538.5 and 466 (or 520 nm). The Pd concn. is calculated from the difference in absorbance at 445 and 538.5 nm. The Pt concn. is determined from the absorbance (at 466 nm) of the combined Pt and Pd concn., or directly from the 520 nm measurement. Copper, Pb, Co, Ni, Fe and Ag do not interfere in amounts < 10 mg.

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
2-(Benzothiazol-2-ylazo)-5-dimethylamino benzoic acid	695 nm $\epsilon=49600$	2.5	To the sample solution containing up to 35 μg of Pd(II), are added 1% Na citrate solution and 3 ml of 0.2M KH phthalate buffer and the pH is adjusted to 2.5 with 10% NaOH solution. Further, 0.7ml of a 0.05% solution of the reagent and 7 ml of acetone are added. The mixture is diluted to 20 ml with H_2O . The absorbance is measured against reagent blank. The 1:1 complex is stable for > 6h. Beer's law is obeyed over the range cited.	207
Michler's thioketone	530 nm $\epsilon=168000$	Acidic	One ml of the test solution is dil. HCl containing up to 10 μg of Pd is treated with 2 ml of acetate buffer solution, 1.5 ml of aq. 3% Triton X-100, 2 ml of ethanolic 0.01% Michler's thioketone and diluted with H_2O up to 25 ml. After 5 min., the absorbance is measured against a reagent blank. The complex formed contains Pd-reagent in the ratio 1:4. Beer's law is obeyed for up to 10	208

µg/ml of Pd. Apart from Au, Hg, Tl, Pt and Ag, no common ion interferes seriously. A method is also discussed to determine Pd in catalysts containing Al, Mg, N, Cu, Fe, Cr, Ca, Pb or Co.

209

Beer's law is obeyed for <12 µg of Pd in 25 ml of solution. The method has been applied for determination of Pd in ores and waste water.

620 nm
ε=90000

2-(3,5-Dibromo-2-pyridylazo)-5-dimethylaminoaniline [4-3,5-dibromo-2-pyridylazo)-NN'-dimethyl-m-phenylenediamine]

210

The ternary complex is formed in acetate buffer medium of pH 6.2. Beer's law is obeyed for up to 16 µg of Pd(II) in 25 ml of final solution. The method has been applied to determine Pd in catalysts and in waste waters.

583 nm
ε=117000

Salicylfluorone [2,6,7-trihydroxy-9-(2-hydroxy phenyl) xanthen-3-one] and hexadecyl trimethyl ammonium bromide

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1-Ethoxy-carbonyl penta-decyl trimethyl ammonium bromide	312 nm	Acidic	Determination of palladium in alumina-based catalysts is described. To 10 g of sample, 10 ml of HNO_3 and 4 ml of conc. HCl are added, the sample is dissolved by heating on a boiling water bath and the solution is made up to 50 ml with H_2O . An aliquot containing 3 to 78 μg of Pd(II) is treated with 2 ml of 0.3M HN_4SCN , followed by 5 ml of 0.1M HClO_4 . The solution is made up to 50 ml and extracted with 10 ml of 5mM reagent in CHCl_3 . The organic phase is dried over Na_2SO_4 (anhydrous). A blank solution containing all the components Pd is similarly prepared. The absorbance is measured against the blank and the Pd content is evaluated from a calibration graph. Hg(III) , Mo(VI) , W(VI) and Os(IV) present in the same amounts as Pd interfere. A 100-fold excess of U(VI) , Cu(II) , Au(III) , Fe(III) or Bi and a 5000-fold excess of Al do not interfere.	211

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-(5-Nitro-2-thiazolyazo) phenol (I)	590nm $\epsilon=35400$	12.4M H_3PO_4	Palladium forms a 1:1 complex with reagent (I) in 12.4M H_3PO_4 containing 10 ppm of the reagent. Beer's law is obeyed for 0.04 to 1.6 $\mu g/ml$ of Pd. Tolerance levels for diverse species (relative to Pd are Co and Ni 10,000; Fe(III) 6000; Cu(II) 5000; Pt 300; Ru 400; Rh 100; Ir 200 and Ag 1000. The method has been used for determining $\approx 3.9\%$ of Pd in a copper sludge, the coefficient of variation being $< 10.5\%$. The reagents (II) and (III) have also been used for determination of Pd under acidic and other conditions identical to those in (I). The λ max values are 590 nm, 645 nm and 630 nm respectively for the Pd complexes with (I), (II) and (III).	212
4-(5-Nitro-2-thiazolylazo) resorcinol(II)	645 nm $\epsilon=21300$			
2,4-Dihydroxy-5-(5-nitro-2-thiazolylazo) benzoic acid (III)	630 nm $\epsilon=19300$			

Name of the Reagent:	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Potassium O,O-Diethyl phosphorodithioate	298 nm $\epsilon = 29000$	2.0-4.0	The pH of the sample solution is adjusted to 2 to 4 with HNO_3 or KOH and sufficient aq. reagent is added to render the final solution 2 mM in the reagent. This solution is diluted to 10 ml with H_2O and extracted with CHCl_3 . The absorbance of the extract is measured against CHCl_3 . Beer's law is obeyed for 1 to 32 μM Pd(II) in the presence of 10 mM EDTA. The lowest tolerance limited in the determination of 24 μM Pd(II) in the presence of 10 mM EDTA are 0.1 mM for Cu , Sn(II) , Sb(III) and NO_2^- , 10 μM for Ag and $< 10 \mu\text{M}$ for Hg(II) , Au(III) and Os(VIII) . Nickel (II) has also been determined with this reagent and the absorbance of the CHCl_3 extract is measured at 385 nm for Ni ($\epsilon = 840$). Beer's law is obeyed for 0.04 to 1.4 mM of Ni(II). The lowest tolerance limits in the determination of 0.92 mM Ni are 1 mM for Mn(II) , Zn , Pb(II) , As(III) , Mo(VI) , W(VI) , V(V) , Cr(VI) , NO_2^- , citrate and	213

oxalate and < 1 mM for Ag, Cu, Co, Hg(III), Sn(II), Sn(V), Bi, Sb(III), Au(III), Fe(III), Se(IV), Te(IV) and Os(VIII).

Di-2-pyridyl ketone
benzoyl hydrazone

H₂SO₄

455 nm
 $\epsilon=9380$

214

The test solution containing < 100 μg of Pd (II) is mixed with 2 ml of H₂SO₄ and 3 ml of 2M NaCl and diluted to 20 ml. The solution is equilibrated with 10 ml of 0.3mM reagent in benzene for 10 min. The absorbance of the organic phase is measured against a reagent blank. Beer's law is obeyed over this range. Iodide, CN⁻, S₂O₃²⁻, thiourea and EDTA must be absent, but H₂, Pb, Fe(III), Sb(III), Ce(IV), Zr and Os(IV) can be masked with tartrate or citrate.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5-(5-Bromo-2-pyridylazo) toluene-2,4-diamine	580 nm $\epsilon=150000$	5.0	Palladium is determined in ores. The sample is digested with HF, HCl and HNO ₃ and the digest is dissolved in 3 ml of 2M HCl. To this solution 2.5 ml of ethanolic 1% dimethyl glyoxime is added and the solution is diluted to 25 ml with 0.1M HCl, and after 20 min., it is extracted thrice with 5 ml of CHCl ₃ . The organic phase is evaporated to dryness. The residue is treated with 0.5 ml of 10% NaCl solution and 5 ml of HNO ₃ , and the solution is evaporated to dryness with 2 ml of conc. HCl. To the solution 2 ml of acetate buffer (pH 5) and 0.4 ml of an ethanolic 0.04% solution of the reagent are added. It is then diluted to 5 ml with H ₂ O. The solution is heated at $\approx 100^\circ$ for 1 to 2 min., 2 ml of 6M HCl is added and the solution is diluted to 10 ml with H ₂ O. The absorbance of the solution is measured against a reagent blank. Beer's law is obeyed for 0.01 to 0.6 ppm of Pd.	215

HSPAF [3-Acetyl-1,5-bis- (2-hydroxy-5-sulpho phenyl) formazan]	532 nm $\epsilon=23000$	Acidic	Palladium forms a 1:1 complex with the reagent in 0.12M H ₂ SO ₄ -0.08M tartaric acid medium. Beer's law is obeyed for <2.8 µg/ml of Pd. Palladium has been determined in carbon-based catalysts also.	216
Propionylpromazine phosphate	495 nm $\epsilon=7100$	2.6	A sample solution of Pd (5 to 525 µg, Walpole buffer solution (pH 2.6) and a 0.2% solution of the reagent are mixed, forming an orange red 1:1 complex. Beer's law is obeyed for 0.2 up to 21 ppm of Pd. Sandell's sensitivity is 22 ng/cm ² . The relative errors are within ± 1.1%. At least 10 µg/ml of Pt(IV) and 140 µg/ml of Os could be tolerated in the determination of Pd; whereas V(V), Ce(IV) and Au(III) interfere. Palladium has been determined in synthetic mixtures, corresponding to Pd alloys used in jewellery. Osmium (VIII) has also been determined with the reagent. For the determination of 5 to 105 µg of Os, the sample solution is mixed with 6M-HCl (to give an overall concn of 0.5 to 2.0M) and aq. 0.2% reagent. The absorbance of the orange red radical cation formed is measured at 510 mµ. Beer's law is obeyed for 0.2 to 4.2 ppm of Os. The Sandell sensitivity and ϵ values are 8 ng/cm ² and 22,100 respectively.	217

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(2-Pyridylazo resorcinol) (I)	550 nm $\epsilon=94000$	5.3	To 2.5 ml of fresh eq. 0.5 mM reagent, 10 ml of acetate buffer (pH 5.3) and 2.5 ml of 10 mM NN'-diphenylguanidine are added. The Pd(II) sample solution is added and the mixture is made up to 25 ml with H_2O . The stirred and set aside for 25 min. The solution is then extracted for 1 min with 10 ml of butanol, the organic phase is separated and the absorbance of the red Pd(II)-(I) chelate is measured against a reagent blank. Sandell's sensitivity is 1.12 ng./cm ² . Palladium can be determined at concn. from 0.21 to 1.91 $\mu g/ml$.	218
Prochlorperazine bis (methanesulphonate)	480 nm $\epsilon=4320$	1.7	Palladium (II) forms an orange-red 1:1 complex with the reagent in the presence of HCl-Na acetate buffer solution. Sandell's sensitivity is 24.62 ng/cm ² . Beer's law is obeyed over the concn. range of 0.4 to 20 ppm of Pd. The reaction is carried out at room temperature and is suitable for the determination of Pd in jewellery alloy.	219

4-(2-Pyridylazo) resorcinol	540 nm $\epsilon=91600$	220	A solution of Pd(II) is extracted with the reagent in the presence of hexadecylpyridinium bromide in CHCl ₃ , and the absorbance of the complex formed is measured. Sandell's sensitivity is 1.16 ng/cm ² . The coloured product is stable for 7h.
Azococsin [7-hydroxy-8-(2-methoxyphenylazo) naphthalene-2-sulphonic acid]	500- 510 nm 4.0	221	The test solution is treated with acetate buffer solution of pH 4 and aq. 0.1M azococsin. The mixture is diluted to a known volume, heated at 80° for 1 h and cooled and the absorbance of the violet complex is measured. Interference is caused by Hg(II), Th, Ce(IV), Fe(III), Sn(II), Bi(III), As, Cu(II), SCN ⁻ and I ⁻ .
5-methyl-2-(2-thiazolylazo) anisole	520 nm 4.0	222	The sample is mixed with 4mM reagent in conc. acetic acid and the pH is adjusted to 4 with acetate buffer. Beer's law is obeyed for 0.06 to 6 ppm of Pd. Tetravalent Pt, Ru(III), Ir(IV), Co, Fe(III), Fe(II), Th(IV), F ⁻ , I ⁻ and EDTA interfere seriously.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Pentane-2,3,4-trione trioxime	270 nm $\epsilon=19100$	4.5-5.6	Complex formation is complete when the reagent is present in 10-fold excess. It is extracted into CHCl_3 -butanol (5:1) and absorbance is measured. Beer's law is obeyed for < 8 ppm of Pd. Interference from Cu, Ni, Fe, Pt, Co, V, Zr, Sn, La and Hg is removed by adding NaF, provided that their molar ratio to Pd is < 100:1. The method has been used to determine Pd in palladized active carbon and a Pd- CaCO_3 catalyst.	223
Thiazole-2-carboxal dehyde-2-quinoyl hydrazone	625 nm $\epsilon=19300$	1M HCl	The sample solution containing up to 42 μg of Pd is mixed with 1M HCl and extracted with 1mM solution of the reagent in benzene, with mechanical shaking. Palladium(II) forms a blue 1:1 complex with the reagent in the benzene extract. Beer's law is obeyed over the range 0.0 to 4.2 $\mu\text{g}/\text{ml}$ of Pd(II). The coefficient of variation for 8 determinations of 20.8 μg of Pd(II) is 0.48%. Iodide, SCN^- , Pt(II) and EDTA interfere and the tolerance limits for Hg(II), Au(III), Ag, Pt(IV), Re, Rh, Ru(III), W(VI), Ir	224

and NO_2^- are low. The method has been applied to the determination of Pd in catalysts, after digestion with aqua regia followed by dissolution in hot 1M HCl.

225

In 1M-HClO₄ medium, reagents (I), (II) and (III) form 1:1 complexes with Pd, while reagent (IV) forms a 2:1 ligand-to-Pd complex. Palladium (2 μM to 0.15 mM) has been determined, with no interference from platinum - group metals. Interference from cations as Cu, La and In is eliminated by use of (II) as the ligand, and that from anions e.g. SO_4^{2-} and NO_2^- is minimized by use of (I) as ligand.

Heterocyclic azo dyes: 3-Hydroxy-4-tetrazolyl azobenzene-2,7- disulphonic acid (I)	665 nm $\epsilon=11000$	1M HClO ₄
3-Tetrazolylazochromotropic acid (II)	640 nm $\epsilon=8000$	1M HClO ₄
3-Hydroxy-4-thiazolyl azobenzene-2,7-disulphonic acid (III)	635 nm $\epsilon=11000$	1M HClO ₄
3-Thiazolylazochromotropic acid (IV)	650 nm $\epsilon=25000$	1M HClO ₄

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Dithizone	635 m μ	3.0-5.0	The separation and determination of palladium and platinum with dithizone using an iodide medium is reported. For the determination of Pd, the sample solution containing Pt and < 40 μ g of Pd, is mixed with 0.1M EDTA. The pH is adjusted to 3 to 5 with 0.1M NaOH, the solution is treated with 1M KI (5 ml) and 0.1M Na ₂ S ₂ O ₅ (0.25 ml), and the mixture is diluted to 10 ml with H ₂ O and extracted for 1.5 min with 10 ml of 0.2 mM dithizone in CCl ₄ . The organic phase is extracted with ammoniacal 0.2% Na ₂ EDTA (2x5 ml) solution. The absorbance of the grey-green Pd dithizonate solution is measured against CCl ₄ . The determination of Pt is carried out in the aqueous phase. To this effect traces of Pd are separated from large amounts of Pt, this involves flotation of sparingly soluble PdI ₂ with benzene. Interference from Fe, Au, Ag, Cu and Bi is avoided by the masking action of F ⁻ and EDTA. The method has been used for determination of Pd in high-purity platinum.	226

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
3,5-Dichlorosalicylaldehyde-4-phenyl-3-thiosemicarbazone (CSAPS)	410 nm $\epsilon=14300$	0.0	The sample solution containing up to 80 μg of Pd (pH adjusted to 0 with H_2SO_4) is shaken for 7 min. with a 0.25 mM solution of the reagent in CHCl_3 . Palladium forms a 1:2 (Pd:R) complex with the reagent, which is extracted into CHCl_3 . The absorbance of the extract is measured against a reagent blank. Beer's law is obeyed for 0 to 8 ppm of Pd. Sandell's sensitivity is 0.0075 $\mu\text{g}/\text{cm}^2$. The coefficient of variation is 0.41% in the determination of 4 ppm of Pd. For 40 μg of Pd there is no interference from up to 500 μg of Cd(II), Co(II), Cr(III), Fe(III), Ir(III), Mn(II), Mo(IV), Ni(II), Os(IV), Pb(II), Rh(III), Ru(III), Ti(IV), and Zn(II). After masking with KSCN, there is no interference from up to 500 μg of Ag, Cu(II), Sc, V(V), Sn(II), or Hg(II) or up to 100 μg of Au(III). The method has been applied to a palladium catalyst containing carbon powder.	227

Name of the Reagen:	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Pot. ethyl xanthate (I)	465 nm $\epsilon=190$	10M HCl pH 8	Palladium (II) forms a 1:2 (Pd:R) complex with various xanthates. The complexes are extracted into CHCl_3 and the absorbance is measured at respective wave length. Beer's law is obeyed for 90 to 500 ppm with (I), 80 to 500 ppm with (III), 80 to 500 ppm with (III), 10 to 15 ppm with (IV) and 80 to 50 ppm with (V). Sandell's sensitivities for (I), (II), (III), (IV) and (V) are 0.58, 0.6, 0.65 and 0.5 $\mu\text{g}/\text{cm}^2$ respectively. Nickel (II) forms a 1:2 (Ni:R) complex with max. absorbance at 415.475 nm. However, Ni has been determined at 415 nm due to higher absorbance with thereagents (I), (II), (III), (IV) and (V). The ϵ values and Sandell's sensitivities ($\mu\text{g}/\text{cm}^2$) are 2900 and 0.02 with (I); 2800 and 0.03 with (II); 3200 and 0.018 with (III); 3100 and 0.02 with (IV) and 3000 and 0.02 with (V) respectively.	228
Pot. propyl xanthate (II)	460 nm $\epsilon=190$	1.0-7.0		
Pot. butyl xanthate (III)	460 nm $\epsilon=176$	2M CH ₃ pH 7		
Pot. benzyl xanthate (IV)	460 nm $\epsilon=182$	1.0-7.0		
Pot. isoamyl xanthate (V)	460 nm $\epsilon=180$	1.0-7.0		

3,5-Diamino-2-(2-thiazolylazo) benzoic acid (I)	575 nm	Aq. HClO ₄	229
3,5-Diamino-2-(4,5-dimethyl-2-thiazolylazo) benzoic acid (II)	605 nm	Aq. HClO ₄	229
		A sample containing Pd is mixed with 12 ml of aq. 70% HClO ₄ for (I) and 7 ml of aq. 70% HClO ₄ for (II) and 2 ml of 1mM (I) or (II) in ethanol and the volume is adjusted to 25 ml with H ₂ O. The absorbance is measured at 575 nm for (I) and at 605 nm for (II). The method has been used to determine 12 to 52 µg of Pd with (I), or 12 to 42 µg of Pd with (II).	
4(5)-D-Arabinofuranose-2:rahydroxybutyl imidazole-2-thione (THBT)	338 nm ε=19900	0.1M HCl	230
		Palladium (II) forms a complex in 0.1M HCl containing a 15-fold molar excess of the reagent. Beer's law is obeyed for up to 5 µg/ml of Pd(II) which forms 1:1, 1:2 and 1:4 complexes with the reagent. In the determination of 2.7 ppm of Pd(II) the coefficient of variation is 1.2% (n=11). Mercury(I), Os(VIII), Ru(IV), Cr(VI), V(V) and S ₂ O ₃ ²⁻ all interfere at 2ppm. The method has been applied to simulated samples of palladiumized CaCO ₃ , active carbon catalysts and to synthetic dental alloy and porpezite.	

Name of the Reagent:	λ_{max} , or working wavelength with ϵ	pH	Remarks	Refs.
4-(2-Pyridyl azo) resorcinol	520 nm $\epsilon=33400$	7.6	The test solution (1 to 5 ml) containing 0.8 to 5.3 mg/l of Pd is mixed with 1 ml of 0.05M EDTA, 2 ml of 1N reagent, 2 ml of 10mM xylose:azoline hydrochloride and 6 ml of pH 7.6 phosphate buffer solution. The solution is diluted to 20 ml, then the Pd complex is extracted into 10 ml of $CHCl_3$, and the absorbance of this extract is measured. Beer's law is obeyed over the cited range. Palladium has been determined in simulated jewellery alloys and stibopalladinite mineral.	231
5-(5-Chloro-2-pyridyl azo) toluene-2,4-diamine	570 nm $\epsilon=69000$	1mM to 0.3M HCl	With this reagent, Pd (in 1mM to 0.3M HCl) and cobalt (in solution of pH 5 to 9) produce purple complexes. Palladium forms a 1:1 complex and Co forms a 1:2 complex with the reagent. The palladium complex is formed slowly but reaction is completed in 10 min. at 70° and 80° and once formed the complex is stable. The Co complex is formed at room temperature in 2 to 3 min. To determine Co plus Pd, the solution is	232

treated with 5 ml of an acetic acid-Na acetate buffer solution of pH 6 and 1 ml of ethanolic 1mM reagent and set aside for 10 min. then 0.3 ml of HCl (1:1) is added, the solution is heated for 10 min. at 70° to 80°, 3.5 ml of HCl (1:1) is added, and the colored solution is diluted with H₂O to 25 ml. The absorbance corresponding to Co plus Pd is measured at 570 nm. Palladium alone is determined by treating a similar amount of solution plus 5 ml of buffer solution with 0.3 ml of HCl (1:1) so that on addition of 1 ml of 0.01M reagent the acidity is too high for formation of the Co complex, and the process is continued as described Beer's law is obeyed for up to 1 mg/l of Pd. In the simultaneous determination of Co and Pd, satisfactory results are obtained at Co-Pd ratios of 1:2 to 1:4 and 2:1 to 5:1. In the determination of 10 µg of Pd there is no interference by 20 mg of Fe(III) or 4 mg of Cu(II). The method is applicable to ore and steel samples.

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Reis.
Pyrimidine-2-thiols: 4,4,6-Trimethyl-1-(2-pyridyl)-1H-4H-pyrimidine-2-thiol (I)	430 nm	dil. HCl	Palladium (II) in dil. HCl is extracted with a 10 mM solution of reagent (I) in butanol and absorbance is measured at 430 nm. Beer's law is obeyed for up to 17.8 ppm of Pd. Palladium has also been determined with (II) by extraction from an acidic solution into a 2.5 mM solution of reagent (II) in CHCl_3 . Beer's law is obeyed for up to 4.0 ppm. Both (I) and (II) are highly selective reagents for Pd, there being no interference from transition metals or from other platinum group metals. Osmium has also been determined with these reagents. With (I) the absorbance is measured at 500 nm for Os. Beer's law is obeyed for up to 27.3 ppm of Os. For the determination of Os with (II), the test solution is treated with 5 ml (II) in acetone, the pH is adjusted to 10.5 and the mixture is diluted to aq. 50% acetone. The absorbance is measured at 400 nm. Beer's law is obeyed for up to 9.2 ppm.	233
4,4,6-Trimethyl-1-(4-phenylthiazol-2-yl)-1H,4H-pyrimidine-2-thiol (II)	430 nm	Acidic		

Bivalent Pd reacts with the reagent to form a 1:2 (Pd:R) complex which is extracted from 5M HCl medium (at pH 2) into CHCl_3 . Beer's law is obeyed for 3 to 25 pp.m. of Pd, and the sensitivity of the method is 0.25 μg of Pd. In the estimation of 450 μg of Pd, the following ions did not cause deviation of more than $\pm 3\%$ in absorbance when present in amounts (mg) shown in parenthesis: Ca(II) (25), Ba(II) (25), Sr(II) (25), Cd(II) (10), Pb(II) (20), Zr(IV) (25), Th(IV) (20), U(VI) (25); Ni(II) (10), Rh(III) (5), Zn(II) (25), Cr(III) (25), Fe(II) (25), Fe(III) (25), Mn(II) (20), Mg(II) (25), Al(III) (25), citrate (40), acetate (50), molybdate (25), fluoride (20), EDTA (10), sulphate (50), oxalate (50), phosphate (50), borate (50), tartrate (50), nitrate (50), Platinon(IV) (1) and Co(III) (4) were tolerated in the system provided the extraction was carried out at pH 2 and 4M HCl respectively. Copper(II) (25) did not interfere in presence of tartrate. Mercury (II) and $\text{S}_2\text{O}_3^{2-}$ interfere.

450 nm
 $\epsilon=3900$

Isonitrosothiocamphor

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
i) N-m-Chlorophenyl-p-methoxybenzohydroxamic acid (m-CMBHA)	400 nm $\epsilon=4700$	3.0	Six hydroxamic acids were screened, out of which m-CMBHA was found to be the most sensitive, details of which have been described. To a portion of Pd solution (85.32 μg) adjusted to pH 3.0 with 0.1M HCl and aq. 0.1M NH_3 ; 10 ml of 0.1% reagent solution in isoamyl alcohol is added. After shaking for 15 min, the phases are allowed to separate and the aq. layer is again extracted with isoamyl alcohol (2 x 2.5 ml) containing the reagent. After dilution of the combined extracts with the solvent, the absorbance of the yellow binary complex is measured at 400 nm. To this extract is added 0.1% 1-(2-pyridylazo)-2-naphthol solution in 95% ethanol before dilution with isoamyl alcohol. The absorbance of the resulting ternary complex is measured at 620 nm. The binary and ternary systems obeyed Beer's law from 12 to 130 and 0.5 to 13 ppm respectively. Fe(III), Ti(IV), Co(II), Ni(II) and V(V) interfere, but they could be masked with ascorbic acid (Fe and V), fluoride(II) and 1,10-phenanthroline (Co and Ni).	235
ii) m-CMBHA + 1-(2-pyridylazo)-2-naphthol	620 nm $\epsilon=12000$	3.0		

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Carboxy-2'-hydroxy-5-methylazobenzene [2-(2-Hydroxyphenylazo)-p-toluic acid]	560 nm $\epsilon=7109$	1.5-3.8	Palladium is determined with 5 ml of reagent solution. Beer's law is obeyed for 0.5 to 13 ppm. Sandell's sensitivity is 15 ng/cm ² . Nickel(II) has also been determined individually with the reagent. Ethanolic 0.1% solution (3 ml) of the reagent is added to 3 ml of Ni solution in ammonium acetate ammonia buffer solution (to final pH < 7.85), plus ethanol to 25 ml. The absorbance is measured at 485 nm ($\epsilon=8300$). Beer's law is obeyed for 0.5 to 7 ppm of Ni. Sandell's sensitivity is 6.9 ng/cm ² . Mn(II), V(V), Ti(IV), Cu(II), Cr(III), Fe(III), Sn(II), Ru(III), Bi(III) and Re(VII) interfere in the determination of both Pd and Ni. to determine Pd(II) and Ni(II) in their binary mixture, 3 ml of 0.1% reagent solution is added to an acidic solution of both metal ions, the pH is adjusted to 2.1 with 0.1M HCl, and the Pd(II) complex is extracted into CHCl ₃ and determined as described. The aq. layer is then analysed for Ni(II).	236

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Tin(II) chloride and Rhodamine 6G (I)	530 nm	Acidic (aq. HCl)	Palladium is determined by reaction with SnCl_2 and Rhodamine 6G (I) in aq. HCl, and flotation of the $[(\text{I}^+)_2\text{Pd}(\text{SnCl}_3^-)_4] [(\text{I}^+)(\text{SnCl}_3^-)]$ complex in di-isopropyl ether. The complex is then dissolved in acetone and the absorbance of the resulting solution is measured. Beer's law is obeyed for 0.05 to 3.5 $\mu\text{g/ml}$ of Pd. The coefficient of variation ($n=7$) is 2.5 to 8.0%. Other platinum group metals and Ag interfere.	237
Potassium iodide-Rhodamine B system	590 nm $\epsilon=650000$		Palladium (II) forms a ternary ion-association with potassium iodide and Rhodamine B in poly-vinyl alcohol. Beer's law is obeyed for $< 80 \text{ ng/ml}$ of Pd.	238
5,5'-[3-(2-Pyridyl)-1,2,4-triazene-5,6-diyl] bis-2-furansulphonic acid disodium salt (Ferene-TM)	432 nm $\epsilon=21700$	1.8-1.9	The reagent, ferene-TM (1mM), forms a yellow 1:2 (Pd:R) complex with Pd in a medium of pH 1.8 to 1.9 (HCl-Na-acetate buffer). Beer's law is obeyed in the range 0.2 to 1.0 ppm of Pd. However Pd can	239

conveniently be detected at the 0.02 ppm level with the reagent. The effect of diverse ions on the palladium-ferene-TM system has been observed with 10 µg of Pd in 25 ml solution. The alkali and alkaline earth metals, even in 20-fold excess, hardly cause any interference. The tolerance limits (in µg) of other cations and anions that do not exceed 3% absorbance variation are mentioned in parentheses: Hg(II) (100), Ni(II) (50), Cr(III) (50), Pb(II) (50), Zn(II) (30), Mo(VI) (50), Pt(IV) (25), Ag(I) (10), Fe(III) (10), Ti(II) (10), Ce(IV) (10), Re(VII) (50), Rh(III) (50), Cl⁻ (20), SO₄²⁻ (200), NO₃⁻ (200), PO₄³⁻ (200), SO₃²⁻ (200), WO₄²⁻ (200) and Cit³⁻ (200). The method has also been applied for determination of Pd in catalysts.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Nitoxime	470 $\epsilon=6900$	1.27	The sample solution is mixed with 5% Triton X-100 solution, the pH is adjusted to 1.27 with 3M HCl and 10mM nitoxime is added. The mixture is diluted to 50 ml and the absorbance is measured after 5 min. Beer's law is observed for < 17 ppm of Pd(II). The coefficient of variation is 0.76% (n=22). Nickel(II) has also been determined with this reagent. In this case the pH is adjusted to 4 to 5 with 1M NH_3 and the absorbance is measured at 555 nm ($\epsilon=6300$). Beer's law is obeyed for < 12 ppm of Ni(II). The coefficient of variation is 0.5% (n=17).	240
K Butyl xanthate	385 nm $\epsilon=13190$	5.2	A sample (≈ 25 ml) is diluted with H_2O (to ≈ 40 ml) and shaken with 3 ml of aq. acetate buffer (pH 5.2) and 2 ml of aq. 0.2% K-butyl xanthate to precipitate the complex. After digestion, a 20% naphthalene solution (2 ml) in acetone is added, the mixture is shaken, and the solid mass is filtered off, washed with H_2O and dissolved in CHCl_3 (to 10 ml), where the absorbance is	241

measured. Beer's law is obeyed for 2.5 to 105.0 μg of Pd in 10 ml of CHCl_3 . Sandell's sensitivity is 8 ng/cm^2 . No anions interfere; the cations Cu(II) , Ni(II) and Hg(II) interfere but these could be masked with EDTA.

Butylrhodamine B and KI	610 nm $\epsilon=1400000$	Palladium forms a water soluble ion-pair complex with KI and butylrhodamine; B in the presence of aacia and Triton X-100. Beer's law is obeyed for 4 to 56 ng/ml of Pd. This is an ultrasensitive method. Gold(III), Ag, Cu(II) and Hg(II) interfere seriously.	242
Thiocyanate and Rhodamine B	590 nm Acidic (H_2SO_4)	To determine 1 to 12 μg of Pd(II) the test solution is treated with 2 ml of 4.5M H_2SO_4 , 1 ml of 30mM KSCN, 1 ml of 4mM Rhodamine B and 0.5 ml of aq. 1% polyvinyl alcohol, then made up to 25 ml with H_2O .	243

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
KSCN and Rhodamine B (C.I. Basic Violet 10)	557 nm $\epsilon=60000$	Acidic (dil. H_2SO_4)	The solution containing Pd is mixed with dil. H_2SO_4 , aq. KSCN, Rhodamine B and H_2O . The mixture is extracted with butyl acetate and the Pd determined in the organic phase. Beer's law is obeyed for 0.1 to 8.8 μg of Pd. The method has been applied to the determination of Pd in dental alloys, organopalladium compounds and hydrogenation catalysts.	244
2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	620 nm $\epsilon=45000$	Acidic	Samples of titanium alloys (10 mg) are dissolved in 2 ml of warm 40% HF_4 solution and to it 3 or 4 drops of conc. HNO_3 , and 3 ml of 40% H_2SO_4 , 3 ml of HF_4 solution, 10 ml of ethanol and 1 ml of ethanolic 0.03% reagent are added. The solution is diluted to 25 ml and after 5 min., the absorbance of 1:2 (Pd:R) complex is measured. Beer's law is obeyed up to 40 μg of Pd. High selectivity is achieved by using HF_4 as a masking agent. In the analysis of synthetic Ti alloys containing 20 μg of Pd(II), the coefficient of variation is 0.8 to 3.3%.	245

4-Salicylamido-1-diacetylmonoxime 3-thiosemicarbazone (SDT)	484 nm $\epsilon=30000$	Alkaline	A 0.2 ml ethanolic solution of Pd (containing 50 $\mu\text{g/ml}$ of Pd(III)) is treated with 2 ml of an ethanolic 0.5% solution of the reagent and 2 ml of 0.5M KOH. The solution is diluted to 10 ml with H_2O and the absorbance of 1:2 (Pd:SDT) complex is measured. Beer's law is obeyed in the range 0.03 to 3.6 $\mu\text{g/ml}$ of Pd. The stability constant is 8.33×10^{10} . Nickel interferes	246
i) Phenothiazine(PZ) ii) Promazine hydrochloride (PMH)	551 nm $\epsilon=3542$ 450 nm $\epsilon=9213$		The sample solution is treated with 3 to 4 ml of ethanolic 0.2% phenothiazine or promazine hydrochloride and diluted to 25 ml with ethanol, and the absorbance is measured at 551 or 450 nm, respectively, against a reagent blank. Phenothiazine forms a violet 1:2 (Pd:R) complex while promazine forms a 1:1 brown complex with Pd(II). The respective Beer's law ranges and Sandell sensitivities are 0.2 to 6.5 and 0.2 to 23 ppm of Pd, and 15.18 and 11.82 ng/cm^2 . For Pd mixed with $\approx 5\%$ of its weight of Ru, the relative error is $< 2\%$. Silver, Au(III), Cu(II), Fe(III), Hg(III) and Pt(IV) interfere.	247

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1-(2-Pyridylmethylene)-5-salicylidene thio carbonohydrazide	505 m $\epsilon=16500$	8.3	The sample solution (containing $< 125 \mu\text{g}$ of Pd) obtained after HNO_3 or aqua regia dissolution is treated with a pH 8.3 buffer solution comprising EDTA, NaOH and H_3BO_3 . After 1 min., 3 ml of 0.1% reagent in dimethylformamide and 5 ml of dimethyl formamide are added and the solution is diluted to 25 ml with H_2O and the absorbance of the orange complex is measured. Sandell's sensitivity is 6.43 ng/cm^2 . In the determination of $0.75 \mu\text{g/ml}$ of Pd the coefficient of variation is $\approx 2\%$. The method has been applied in the determination of Pd in hydrogenation catalysts and carbencillin.	248

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Glyoxal bis- (4-phenyl thiosemicarbazone) (GBPT)	635 nm $\epsilon=3200$ 700 nm $\epsilon=1500$	9.6-1N	The green 1:1 Pd(II)-GBPT complex is formed between pH 9.6 and 1N acidity. The solution containing 50 to 500 μg of Pd is adjusted to pH 1.8 to 2.0, then mixed with 2 ml of 0.1% reagent solution in DMF, 13 ml of DMF and diluted to 25 ml with water. After a few minutes, the absorbance is measured against a solvent blank. Beer's law is obeyed over the range 2.5 to 20 ppm of Pd. the coefficients of variation at the levels of 10 ppm at pH 2.2, and 5 ppm in 0.4N H_2SO_4 are 1.04 and 0.83%, respectively.	249

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4,4,6-Trimethyl-1-phenyl (1H, 4H)-pyrimidine-2-thiol	430 nm $\epsilon=4066$	4.6-6.5	A 5 ml portion of the reagent in DMF is added to a solution containing 3 to 25.5 ppm of Pd, which is then diluted to ≈ 30 ml with water. The pH is adjusted with HClO_4 and NH_3 (pH 6.5 max) and 2 ml of buffer solution (pH 4.6) is added. Naphthalene (2 g) is added to the solution at 60° , which is then heated to $85^\circ\text{-}90^\circ$ and stirred. The naphthalene containing the metal complex is then separated by cooling and is finally dissolved in CHCl_3 to give a volume of 10 ml. The absorbance of the CHCl_3 solution is measured. Beer's law is obeyed over the range 3.0 to 25.5 ppm of Pd. Sandell's sensitivity is 26 ng/cm^2 . For 15 ppm of d, the coefficient of variation is 0.94%. Iridium (3.8 to 42 ppm) has also been determined with this reagent in the pH range 2.5 to 4M HClO_4 . The absorbance is measured at 430 nm. Beer's law is obeyed over the concentration range 3.8 to 42 ppm for Ir. The ϵ value and Sandell's sensitivity are 3879 and 49 ng/cm^2 respectively. For 23	250

ppm of Ir the coefficient of variation is 0.60%.

251

The reagent forms a green 1:1 complex with Pd(II) at low pH in 0.28 to 1.14M HCl and a brown 1:2 (Pd:R) complex at pH 8 to 9.5. Aliquots containing 13 to 67 μg (for the brown complex) or 34 to 182 μg (for the green complex) of Pd(II) are added to a 10-fold excess of 2.5mM reagent in DMF. The pH for the brown complex is adjusted with dil. HCl or NaOH. The solution is heated on a boiling water bath for ≈ 10 min., cooled and diluted to 10 ml to give an approx. 70% DMF medium. For the green complex, 1 ml of 5M HCl is added before dilution. Absorbance is measured at 540 or 590 nm for the brown or green complex, respectively. Beer's law is obeyed for up to 23.4 and 7.2 ppm and the corresponding Sandell sensitivities are 0.025 and 0.0033 $\mu\text{g}/\text{cm}^2$ for green and brown complexes respectively.

Phenanthrenequinone
monothiosemicarbazone

540 nm
 $\epsilon=12700$

590 nm
 $\epsilon=4200$

8.0-9.5

0.28-
1.14M
HCl

Name of the Reagen.	λ_{max} or working wavelength with ϵ	pH	Remarks	Ref's.
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Dianthipyrylthiourea	345 nm	Ammoniacal	A sample (10 ml) of electrolyte containing ≈ 20 g/l of $PdCl_2$ is diluted to 250 ml with aq. 0.1M NH_3 and a portion (5 ml) of the solution is diluted to 100 ml with H_2O . A portion (3 ml) of this solution is mixed with 0.5M EDTA (2 ml), 0.1M ascorbic acid (2 ml), H_2O (10 ml) and conc. aq. NH_3 (3 ml) and the Pd is extracted into 0.02M reagent in $CHCl_3$ (15 ml). The extract is made up to 25 ml with $CHCl_3$ and its absorbance is measured against a reagent blank. In the presence of EDTA, Ca, Mg, Co, Ni, Zn, Cd, Mn, Pb and Cu are not extracted, and in the presence of ascorbic acid, the Pt-group metals do not interfere.	252
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Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-Methoxydithiobenzoate	425 nm	3.0-7.0	Palladium forms a 1:2 complex with the reagent in an aq. medium of pH 3 to 7 which is extracted into CHCl_3 . Beer's law is obeyed for 0.1 to 4.5 $\mu\text{g/ml}$ of Pd. Ruthenium (III) has also been determined with the reagent and forms a $\text{Ru(III)-EDTA-4-methoxydithiobenzoate-diphenyl-guanidine(1:1:1:2)}$ complex in an aq. medium of pH 3 to 7. The complex is extracted into 3-methylbutan-1-ol- CHCl_3 (3:7), and exhibits λ_{max} at 498 nm ($\epsilon=8400$). Beer's law is obeyed for 0.5 to 15.5 $\mu\text{g/ml}$ of Ru (III). For simultaneous determination of Pd (II) and Ru(III) the Pd is initially extracted into the reagent, then the aq. phase is treated with diphenyl-guanidine and Ru is extracted. The coefficient of variation is $< 1.8\%$ ($n=5$) when determining ≈ 5 to 43 μg of Pd in prepared mixtures.	253

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Malachite green (C.I. Basic green 4) and KSCN	630 nm	2.0	A solution of Pd and Pt is treated with KSCN and a solution of malachite green at pH 2 and room temperature to form a Pd complex, which is extracted into benzene, toluene or xylene. The aq. solution is then heated to 85° to form the corresponding Pt complex, which is likewise extracted. The absorbances of both organic phases are measured at 630 nm, and the conc. of each metal is read from a calibration graph. Gold interferes with Pd determination. The method is only applicable to a Pd:Pt ratio between 50:1 and 1:150. In analysis of a Pd-Pt concentrate containing 26.8% of Pd and 5.8% of Pt by weight, accurate results are obtained, with coefficients of variation of 1.7% and 8.3% respectively (n=5).	254

Name of the Reagent	λ max or working wavelength with ϵ	pH	Remarks	R:fs
2-(5-Bromo-2-pyridyl azo)-5-(diethylamino) phenol	585 nm $\epsilon=38600$	3.53	When a 50% ethanolic solution containing < 50 μg of Pd(II) is treated with the reagent a violet complex is formed, the absorbance of which is measured. Beer's law is obeyed for up to 50 μg of Pd(II) with a coeff. of variation of < 0.4%. Up to 5 mg of Pt and 0.3 mg of Au(III) do not interfere, whereas Cr(VI), Fe(II) and Th(IV) do.	255

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Cyclohexyl thiolglycolate [mercaptoacetate] (CyHTG)	385 nm $\epsilon=16700$	4.0	The test solution is treated with 1 ml of ethanolic 0.1% reagent, the pH is adjusted to 4 with acetate buffer solution, and sufficient 1M KNO_3 is added to make its final concn. 0.1M in 10 ml of solution. This solution is extracted with 10 ml of CHCl_3 and the absorbance of the dried (Na_2SO_4) extract is measured. Beer's law is obeyed for 1.12 to 37.1 μg of Pd in 10 ml of final solution. Sandell's sensitivity is 6.4 ng/cm^2 . Nickel(II) has also been determined with this reagent. The test solution is treated with 1 ml of ethanolic 0.1% reagent, the pH is adjusted to 8 for Ni with acetate buffer solution and sufficient 1M KNO_3 is added to make its final concentration 0.1M in 10 ml of solution. This solution is extracted with 10 ml of CHCl_3 , and the absorbance of the dried (Na_2SO_4) extract is measured at 410 nm for Ni ($\epsilon=4440$). Beer's law is obeyed for 5.9 to 70.8 μg of Ni in 10 ml of final solution. Sandell's	256

sensitivity is 13.3 ng/cm² for Ni. Nickel and Pd can be simultaneously determined in some alloys by this method; the sample being initially dissolved in HCl-HNO₃.

N-Naphthyl-N -
pyridylthiourea

390 nm
ε=34000

2 0-2 5

257

For determination of Pd(II) the test solution is adjusted to pH 2.0 to 2.5 with HCl. A solution of the reagent in 70% ethanol is added; the solution is diluted to a known volume and the absorbance is measured against a reagent blank. Beer's law is obeyed for 1.3 to 12 ppm of Pd. Silver, Pb(II) and Au(III) interfere. In the determination of 3 ppm of Pd in the presence of 1 ppm each of Rh, Ru, Ir and Pt, the standard deviation is 0.035 ppm (n=10).

Name of the Reagent	λ max. or working wave-length with ϵ	pH	Remarks	Refs.
4-Hydroxy-3-methoxy benzaldehyde thiosemicarbazone	368 nm	3.65	The test solution containing 1 to 60 μ g of Pd(II) is treated with 5 ml of buffer solution (HCl-Na acetate of pH 3.65), 6 ml of ethanol and 4 ml of 0.3% solution of the reagent in 85% ethanol. The mixture is diluted with H ₂ O to 25 ml and its absorbance is measured. Beer's law is obeyed over the cited range. Sandell's sensitivity is 4.22 ng/cm ² . The standard deviation for 1.5 ppm of Pd is 6.6 ppb. Copper (II) (2.5 to 80 μ g) has also been determined at 410 nm with this reagent at pH 11.98 (KH ₂ PO ₄ -Na acetate buffer). Sandell's sensitivity is 5.15 ng/cm ² . The standard deviation for 1.5 ppm of Cu is 1.7 ppb (n = 10).	258
4-(2-Pyridylazo) resorci- nol. (FAR) and hexadecyl trimethyl ammonium bromide	540 nm ϵ =28600	5.0-8.0	The ternary complex is formed optimally at pH 5.0 to 8.0. Beer's law is obeyed for 0 to 3/6 μ g/ml of Pd.	259

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Dibenzyl ditlthio-oxamide	454 nm	Acidic	A 0.1 g sample (crude silver) is heated with HNO_3 , the mixture is filtered, concentrated, and 2 ml of ethanolic 1% succino-ketoxime is added. The Pd complex formed is extracted with CHCl_3 , 1 ml of butanoic 0.6% reagent and 20 ml of 8.4M HCl are added, and the Pd complex with the reagent is extracted into CHCl_3 . Recovery of Pd is > 90% and 1000-fold amounts of Pb, Cu, Ni and Zn do not interfere.	260
KI	408 nm 480 nm	HCl medium	Palladium (II) reacts with KI in HCl medium (10% V/V) to form a red complex ion (PdI_4^{2-}) with two absorbance maxima at 408 and 480 nm. Ascorbic acid removes the iodine colour and masks interference from other elements, e.g. Au, Fe and V, in alloy solution. The method is simple and accurate and has been used to determine 0.5 to 6% of Pd(II) in Au-based alloy with satisfactory results.	261

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
N-Benzoylaminothioformyl-N'-phenyl hydroxylamine [N'-benzoyl-N-hydroxy-N'-phenyl-2-thiourea]	425 nm	4.5	A solution of Pd (50 ppm; 1 to 15 ml) is diluted to 40 ml and treated with 2.5 ml of 1M acetate buffer (pH 4.5) and 2 ml of a 0.2% solution of the reagent in ethanol. The mixture is kept at room temperature for 15 min., then 2 ml of 20% naphthalene solution in acetone is added, with vigorous shaking for 60s. The cryst. naphthalene with the absorbed Pd complex is filtered off, washed with H ₂ O, dried, dissolved in DMF (to 10 ml) and the absorbance is measured against reagent blank. Beer's law is obeyed for 5 to 50 $\mu\text{g/ml}$ of Pd in the DMF solution.	262
Indane-1,2,3-trione monosemicarbazone	360 nm $\epsilon=7210$	4.0-5.5	The reagent forms a 1:1 complex with Pd (II) in acetate buffer. Beer's law and optimum concn. ranges and standard deviation are 0.85 to 7.66 ppm, 1.70 to 5.96 ppm and 0.0431. Copper(II) has also been determined with this reagent. The reagent forms a 1:2 (Cu:R) complex with Cu(II) and has λ max at 355 nm ($\epsilon=12,500$). Beer's law,	263

optimum concentration ranges and standard deviation are 0.32 to 3.49 ppm, 0.95 to 3.17 ppm and 0.0089. Simultaneous determination of Cu and Pd are made by measuring the absorbance at both λ_{max} with and without masking of Pd with SCN^- . The error is $\pm 2\%$. Fluoride, Cl^- , Br^- , I^- , NO_3^- , PO_4^{3-} , ClO_3^- , BrO_3^- , citrate, tartrate, oxalate, tetraborate, borate, Sr and Zr(IV) do not interfere.

264

The complex is formed in phthalate buffer medium (pH 3.0) containing 0.3 to 10mM Cl^- and extracted into CHCl_3 . Beer's law is obeyed for 1 to 8 ppm of Pd(II) and the detection limit is 0.16 ppm. Tolerance levels in the determination of 4.65 ppm of Pd(II) are e.g., < 1 ppm of Cu(II), Au(III), SCN^- or I^- ; 2 ppm of Bi, Sn(II), Rh(III), Ga or oxalate; and 5 ppm of Mo(VI), Fe(III), W(VI), Br^- , NO_2^- and PO_4^{3-} .

30

2-(2-Picolyliminomethyl)
pyrrole 2-(2-pyridyl
methyl)iminomethyl)
pyrrole]

400 nm
 $\epsilon=9500$

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-Methyl-1,4-naphthoquinone-4-oxime	460 nm	6.5-7.8	The reagent forms a yellow 1:1 water insoluble complex with Pd(II), but extractable with butanol. Within the optimum pH range, 6.5 to 7.8, Beer's law is obeyed up to 11.9 ppm of Pd(II) and the corresponding optimum analytical range is 1.6 to 10.5 ppm. For 5.3 ppm of Pd(II), the respective relative errors are 0.46%. Os(VIII) and Ir(III) have also been determined with this reagent. The reagent forms brown 1:2 (M:R) complexes with both Os(VIII) and Ir(III), that are insoluble in H ₂ O but extractable with butanol. The λ max for Os(VIII) and Ir(III) complexes occur at 460 and 450 nm, respectively. Within the optimum pH ranges 6.5 to 7.7 for Os(VIII) and 5.9 to 7.3 ppm for Ir(III), Beer's law is obeyed up to 29.5 and 13.7 ppm for Os(VIII) and Ir(III) respectively. For 9.5 ppm of Os(VIII) and 6.4 ppm of Ir(III), the respective relative errors are 0.44% and 0.57%.	265

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5,6-Dimethyl-2-nitroindan -1,3-dione dithiosemicarbazone (NDIDT)	480 nm $\epsilon=16000$	4.5	To a solution containing 10 to 95 μg of Pd, 2.5 ml of dimethylformamide, 3 ml of $5 \times 10^{-3}\text{M}$ NDIDT and 10 ml buffer (pH 4.5 for Pd) are added and the solution is diluted to 25 ml with water to give an orange red 1:2 (Pd:R) complex. Beer's law is obeyed for Os(VIII) have also been determined with this reagent. The absorbance of Co(II) and Os(VIII) is measured at 420 nm ($\epsilon=15000$) and 490 nm ($\epsilon=13000$) respectively. The ligand forms 1:2 (Co:R) brown complex with Co(II) and 1:4 (Os:R) brown complex with Os(VIII). Beer's law is obeyed for 0.24 to 2.40 and 0.76 to 7.61 ppm for Co(II) and Os(VIII) respectively.	266

Name of the Reagent	λ_{max} or working wave-length with ϵ	pH	Remarks	Refs.
3-Hydroxy-2-methyl-1, 4-naphthoquinone-4- oxime	485 nm $\epsilon = 18,600$	4.0-6.0	Palladium solution (containing 4.1 to 67.8 μg of Pd) is mixed with 0.5 ml of 5mM reagent and the solution is buffered to pH 4 to 6. The mixture is heated to 60° and the complex is extracted with molten naphthalene. The solid formed is dissolved in DMF and the absorbance of the solution is measured. The optimum range is 0.41 to 6.78 ppm of Pd. Sandell's sensitivity is 0.0056 $\mu\text{g}/\text{cm}^2$. The method has been applied for the determination of Pd in synthetic samples, alloys and catalysts.	267

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(2-Pyridylazo) resorcinol(I) and Xylometazoline hydrochloride (II)	520 nm $\epsilon=33400$	7.6	Titanium alloy (0.5 g), containing 0.1 to 0.8% of Pd, is dissolved by warming in 6M HCl and HBF ₄ , then conc. HNO ₃ is added dropwise to oxidise the Ti. The solution is diluted to 100 ml, keeping the HCl concn. at 2.5 M. An aliquot containing 5 to 50 μ g of Pd is mixed with 0.01M EDTA and the solution is neutralized with 0.1M NaOH. Phosphate buffer solution (pH 7.6), 1mM-(2-pyridylazo) resorcinol (I) and 0.01M-xylometazoline hydrochloride (II) are added, and the mixture is mixed with CHCl ₃ for 1 min. The absorbance of the pink organic layer, containing the Pd(II)-(I)-(II) complex is measured. Titanium at < 20 mg/l or 5 to 50 μ g of Pd did not interfere. Best law is obeyed for 0 to 5 μ g/ml of Pd. The coefficient of variation is 5%.	268

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
4-(2-Pyridylazo) resorcinol	464 nm $\epsilon=5080$	Acidic	Methods for the determination of Ir, Rh, Pt and Pd when present together are described. The sample solution is mixed with 5 ml of 0.03M HCl, 0.8 ml of 0.1M EDTA and 0.5 ml of 0.1% reagent and H ₂ O to 50 ml. After extraction with ethyl acetate (25 ml), the absorbance of the organic phase is measured against reagent blank. Similarly, an aliquot (10 ml) of sample solution is mixed with 10 ml of HClO ₄ , 3 ml of SnBr ₂ solution and H ₂ O to 25 ml. After setting aside for 30 min., the absorbance of the Pd-SnBr ₂ complex formed is measured at 430 nm against a reagent blank. Similarly, absorbance of Rh-SnBr ₂ and Pt-SnBr ₂ complexes are measured at 516 and 650 nm respectively. Finally 1 ml of 0.03M HCl, 0.15 ml of 0.1M EDTA, 0.03 ml of 0.1% reagent solution and 7 ml of BaBr ₂ solution are added to 10 ml of sample solution and the mixture is heated for 40 min. The mixture is further heated with 5 ml of SnBr ₂ solution for 1 min.	269

After cooling, H_2O is added to 25 ml and the absorbance of the $Pd-SnBr_2$ and $Ir-SnBr_2$ complex is measured at 402 nm against a reagent blank. From these absorbances, contents of the cited elements are calculated.

Salicylfluorone and
hexadecyltrimethyl
ammonium bromide

588 nm
 $\epsilon=110,000$

5.5-7.0

270

The ternary complex between Pd , salicylfluorone and hexadecyltrimethyl ammonium bromide is formed in a medium of pH 5.5 to 7.0. Beer's law is obeyed for up to 0.56 $\mu g/ml$ of Pd in the final solution. The complex has been used in the determination of Pd in active carbon based catalysts.

Name of the Reagent:	λ max. or working wavelength with ϵ	pH	Remarks	Ref.
Dibromophenylfluorone in presence of hexadecyltrimethyl ammonium bromide	610 nm $\epsilon=71000$	6.0	A 0.25 g sample of catalyst (Pd on alumina) in 10 ml of aqua regia is evaporated to dryness followed by treatment of the residue (thrice) with conc. HCl to remove N oxides and dissolution in dil. HCl to 50 ml. A portion of this solution is made just alkaline to phenolphthalein with 0.1M NaOH and 3 ml of 0.05% NaF, 6 ml of 2% hexadecyl trimethyl ammonium bromide, 0.6 ml of 1mM dibromophenyl fluorone, 5 ml of phosphate buffer (pH 6) and H_2O to 25 ml are added. The absorbance is measured against a reagent blank after 30 min. Beer's law is obeyed for $< 20 \mu g$ of Pd in 25 ml of solution. Interference from Au, Fe(III), Al, Ti and Cu is observed; however, Al and Cu could be masked. The method has also been used to determine Pd on activated charcoal.	271

T(4-TMAP)P [5,10,15 20-Tetrakis-(3-trimethyl ammonium)-porphine]	433 nm $\epsilon=250000$	5.0	The solution (5ml) of Pd in acetate buffer of pH 5 is treated with 2 ml of the reagent solution in the presence of 1 ml of 4% ascorbic acid solution and 5 ml of ethanol. After 2 min., 2 ml of H ₂ SO ₄ (1:1) is added; the resulting complex is stable for > 30 min. Beer's law is obeyed for 0 to 0.4 $\mu\text{g/ml}$ of Pd. The coefficient of variation is 1.6%.	272
4,4'-Bis(dlethylamino)- thiobenzophenone (TEDAT)	535 nm $\epsilon=210000$		Palladium or mercury forms a purple 1:4 (M:R) complex with 0.02% TEDAT in presence of phosphate buffer solution. Triton X-100 and Na dodecyl benzene-sulphonate. Both Pd and Hg ($\epsilon=207000$) are determined at 535 nm and Beer's law is obeyed for up to 10 μg of Pd/25 ml and up to 25 μg of Hg/25 ml.	273
5-(2-Thiazolylozo) toluene-2,4-diamine	590 nm $\epsilon=57000$	strongly acidic	The reagent forms a 1:1 blue complex with Pd in a strongly acidic medium and is stable for 24 h. Beer's law is obeyed for up to 7 μg of Pd in 5 ml of solution.	274

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
[3-(2-Furyl)-N-(4-methoxyphenyl)-acrylohydroxamic acid] and 5-diethylamino-2-(2-pyridylazo) phenol.	560 nm $\epsilon=1000$	3.0	Determination of Pd in environmental samples is reported. Bivalent Pd (5 to 40 μ g) is selectively extracted from aq. solution (5 ml; pH3) into a 0.05M solution of the reagent in isoamyl alcohol (2x10 ml). The combined extracts are further shaken with 5M HCl (5 ml) and ethanolic 1mM 5-diethylamino-2-(2-pyridylazo) phenol (2.5 ml). The absorbance of the green extract of the resulting ternary complex is measured. No interference due to other Pt metals is observed. The method has been applied for the determination of Pd in catalysts, in biological materials and in fresh water.	275
Mandelazo I [2-[2-(4,5-Dihydro-3-methyl-5-oxo-1-phenyl-1H-pyrazol-4-yl) phenyl] -2-hydroxy acetic acid]	300 nm	Acidic	A portion of the test solution of Pd (II) is mixed with 2 ml of methanolic 5mM Mandelazo I and 2% HCl and diluted to 10 ml. Beer's law is obeyed from 0.2 to 6.4 μ g/ml of Pd. Iron (III) and Pt(IV) have also been determined with the reagent. A portion of the test solution of Fe(III) or	276

Pt(IV) is mixed with 2 ml of methanolic 5mM Mandelazo 1 and 5 mM Na₂B₄O₇ buffer solution (pH 3.8 for Fe or 8.0 for Pt) and diluted to 10 ml. The λ_{max} occurs at 295 and 287 nm for the Fe and Pt complex respectively. Beer's law is obeyed from 0.25 to 7.0 and 1.5 to 42 $\mu\text{g/ml}$ of Fe and Pt respectively. Palladium and Fe(III) can be determined in the presence of 5-fold (or greater) conc. of Mn(II), Cd, Hg(II), Zn and Al; tolerance levels are less for Co, Ni, Cu, Be, Th and U.

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The water insoluble reagent forms a complex with Pd(II) in presence of Na dodecyl sulphate at pH 3.4. The Soret band of the complex lies at 416 nm, well separated from the bank (at 443 nm) of the diacid form of the reagent below pH 2.4. The complex is stable for > 20 h. Beer's law is obeyed for up to 250 ppb of Pd.

3.4

416 nm
 $\epsilon=120000$

5,10,15,20-Tetrakis-
(4-acetoxyphehyl)
porphine

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
5-(8-Quinolylazo)-2-thioxothiazolin-4-one	280 nm $\epsilon=25000$ 507 nm	6	The reagent forms a red 4:1 (R:Pd) complex, at pH 6.14 and Pd is determined in traces at either 280 or 507 nm.	278
NN-dimethyl-4-nitro aniline (I) and Bromocresol purple(II)	505 nm $\epsilon=96000$	4.0	A sample of Pd on activated charcoal is digested with $\text{HClO}_4\text{-HNO}_3$ (1:1) and evaporated repeatedly with conc. HCl to remove HNO_3 . The residue is dissolved in a small volume of HCl and diluted with H_2O . An aliquot of the solution is mixed with 1.5 ml of ethanolic 3.3 mM reagent (I), 10 ml of aq. 0.2mM of reagent (II) and H_2O to 20 ml. Aqueous NH_3 is added dropwise until the solution turns reddish orange. The solution is decolorized with dil. HCl, 1 ml of Na-acetate-HCl buffer (pH 4.0) is added, the solution is extracted with CHCl_3 and absorbance of the extract is measured. Recovery is 95 to 105%. Beer's law is obeyed for 1 to 8 μg of Pd in 10 ml of solution; the molar ratio of Pd: (I): (II) in the ternary complex is 1:2:2. Sandell's sensitivity is 1.1 ng/cm^2 . The method has been applied for determination of traces of Pd on alumina.	279

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
2-(5-Bromo-2-pyridyl) azo-5-diethylamino phenol (5-Br-PADAP) and Triton-X-100	536 nm $\epsilon=175000$	0.1N H_2SO_4	Micellar solubilization photometric determination of micro amounts of palladium has been reported. Standard solution containing up to 10 μg of Pd is titrated to a pink colour with 0.01N NaOH with phenolphthalein as indicator. To it are added 2 ml of 0.1N H_2SO_4 , 6 ml of a 0.8% solution of the reagent (5-Br-PADAP) in ethanol, and 3 ml of aq. 10% Triton-X-100. After diluting the mixtures to 25 ml with H_2O , absorbance is measured. Beer's law is obeyed up to 0.4 $\mu g/ml$ of Pd, Iron(III), Co(II), Ni(II) and Au(III) interfere seriously and must first be separated.	280

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Thiocyanate and tetrabutyl ammonium ion	310 nm 475 nm	1.5-8.0	The Pd(II) -SCN ⁻ complex forms a water soluble ion pair with tetrabutyl ammonium in CHCl ₃ . Under the optimum conditions of pH 1.5 to 8.0, $\approx 0.5M$ SCN ⁻ and 0.06 to 0.1M tetrabutylammonium in the presence of 0.1M F ⁻ , the extraction efficiency of the ion pair is $\approx 99.5\%$. Beer's law is obeyed for 5 to 60 μM Pd at 310 nm and for 0.3 to 3mM Pd at (475 nm). The coefficient of variation ($n=15$) is 0.58% for 53.2 μg of Pd and the sensitivity at 310 nm is 3.7 ng of Pd.	281
2-allylthiourea and thiocyanate	390 nm	5.0	The sample solution containing Pd is mixed with 1M EDTA, 1M 2-allylthiourea, 1M SCN ⁻ aq. NH ₃ -acetic acid buffer solution (pH 5) and 3-methylbutanol. After 3 min. the absorbance of the organic layer is measured. Beer's law is obeyed for 1 to 32 ppm of Pd. The coefficient of variation is 3.7%. Platinum(II) has also been determined with this reagent. The absorbance is measured at 500 nm for Pt(II). Beer's law is obeyed for 3 to 98 ppm of Pt. The coefficient of variation is 2.82%.	282

Indane-1,2,3-trione trifluoromethane	320 nm $\epsilon=15600$	40	283	A solution containing 5.3 to 63.8 μg of Pd (II) is treated with 2 ml of 0.01M reagent in acetate buffer medium of pH 4.0, then diluted to 25 ml, and the absorbance is measured. At 1.34 ppm in the final solution, the coefficient of variation ($n=10$) is 1.75%. The colour is stable for 1h. Copper(II) interferes while Fe(III), Co, and Ni have been masked with F ⁻ .
Indane-1,2,3-trione monothiosemicarbazone	460 nm $\epsilon=15000$	30	284	The reagent forms a 1:1 complex with Pd (II) at pH 3.0. Beer's law is obeyed for 0.42 to 3.63 ppm of Pd. Up to 2 ppm of Cu(II) can be tolerated in the determination of Pd by masking with Na ₂ S ₂ O ₃ . Copper(II) has also been determined with this reagent. The reagent forms a 1:2 (Cu:R) complex with Cu(II) in acidic medium (0.32M HCl). The absorbance is measured at 430 nm ($\epsilon=17600$). Beer's law is obeyed for 0.25 to 2.03 ppm of Cu. The method has been applied for determination of Cu in alloy steels and sheep liver.

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Picoulinam/doxime	370 nm $\epsilon=4900$	2.0	The solution of 50 to 370 μg of Pd(II) is treated with 1 ml of 0.1M reagent and 3 ml of ethanol, then diluted to 10 ml with Britton-Robinson buffer solution of pH 2.0. The absorbance of the solution is measured against a reagent blank. The metal to ligand ratio in the complex is 1:2. Iron, Au(III) and V(V) interfere. This method has been used to determine Pd ($\approx 10\%$) in catalysts based on BaSO_4 , Al_2O_3 and CaCO_3 .	285
Furylacrolein [3-(2-furyl)prop-2-enal] oxime (FAO)	360 nm $\epsilon=85000$	5.0	The test solution is treated with 2 ml of 1mM FAO in aq. 20% ethanol, adjusted to pH 5.0 with acetate buffer solution and, after 10 min. extracted with 5 ml of CHCl_3 by shaking for 1 min. The absorbance of the extract is measured against a reagent blank. Beer's law is obeyed for 1 to 10 μM Pd in the extract. The method has been applied for the determination of Pd in $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ based minerals.	286

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
1,2-Diaminoanthraquinone β -chlorodextri	660 nm $\epsilon=32500$	NH ₄ Cl-NH ₃ buffer (pH 10.3)	To a solution of Pd(II), 4 ml of aq. 0.1mM reagent, 2 ml of NH ₄ Cl-NH ₃ buffer solution (pH 10.3), 0.4 ml of 5% ascorbic acid solution and H ₂ O to 10 ml are successively added. The absorbance is measured and the first derivative spectrum is recorded. Beer's law is obeyed for 36 to 3000 and for 50 to 1800 ng/ml by the normal and derivative techniques, respectively; and corresponding detection limits are 11 and 14 ng/ml. The coefficients of variation are 2.1 and 1.7% respectively.	287
2-Hydroxy-4-methoxy-5'-chlorochalcone oxime 3-(5-Chloro-2-hydroxyphenyl)-1-(4-methoxyphenyl) prop-2-en-1-one oxime	380 nm $\epsilon=7900$	2.5	Palladium(II) is extracted into a 5mM solution of the reagent in isobutyl alcohol from aq. solution at pH 2.5. The absorbance of the extract is measured; it remained stable for > 72 h. Beer's law is obeyed in the range 14 μ M to 1.95mM Pd. Gold(III), Cr(III), Zr and EDTA interfere strongly.	238

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
O,O'-Diaminoazobenzene [azobenzene-2,2'diamine]	585 nm $\epsilon=16625$	2.0	To a solution containing Pd(III) are added 1 ml of ethanolic 2.8mM reagent, 10 ml of Prdeaux buffer solution (pH 2), and H ₂ O to 20 ml. 3-Methylbutan-1-ol (10 ml) is added, with shaking for 5 min., and after a further 5 min. the organic phase is filtered and the absorbance is measured. Beer's law is obeyed for 0.5 to 5 ppm of Pd, and the coefficient of variation (n=11) at 3 ppm of Pd is 0.18%.	289
Tin(III) chloride crystals violet (C.I. Basic Violet 3) in presence of polyvinyl alcohol	550 nm $\epsilon=3700000$	Acidic	Palladium is determined as its ternary complex in which the optimum working concn. are 0.12 to 0.14M SnCl ₂ , 1.2 to 1.6 mM crystal violet, 0.33 to 0.35M HCl and 0.24 to 0.64% poly-vinyl alcohol. Beer's law is obeyed for 0.1 to 1.0 μ g of Pd in 215 ml of final solution. The method is used to determine Pd in some precious metals.	290

5-Salicylidene rhodanine	450 nm	3.6	291
The solution of Pd (12.5 to 125 µg) is treated with 3 ml of 0.1% reagent in DMF, 2 ml of acetate buffer solution of pH 3.6 and 1 ml of 1M KNO ₃ . The mixture is diluted to 25 ml with H ₂ O and its absorbance is measured against a reagent blank. Beer's law is obeyed for 0.5 to 5 ppm of Pd, and the error is ±0.5%. In the determination of 2 ppm of Pd, interference is caused by 4 ppm of Zr, Mn(II), Fe(III), Co, Al, Sn(II) or Hg(II); 6 ppm of Ag and 8 ppm of Ga or In.			
1-Methyltriazol-diethylazoaniline [NN-diethyl-4-(4-methyl-1,2,4-triazol-3-ylazo)aniline]	620 nm	1.5-2.0	292
To a 1mM solution of the reagent in dil. acetic acid (pH 4 to 4.5) are added ethanol and PdCl ₂ in HCl. Beer's law is obeyed up to ≈80 µM. Copper(II), Hg(I) and Hg(II) have also been determined with this reagent. To a 1mM solution of the dye in dil. acetic acid (pH 4 to 4.5) are added ethanol (or H ₂ O for Hg(II) determination) and one of the following solutions: Cu acetate in DMF (pH6), Hg ₂ (NO ₃) ₂ in HNO ₃ -ethanol (1:4, pH ≈ 3) or aq. HgCl ₂ (pH 5). The absorbances are measured at 538, 500 or 505 nm for Cu, Hg(I) or Hg(II) respectively.			

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
Methylglyoxal bis-(4-phenyl-3-thiosemi carbazone)	606 nm	9M H_2SO_4	The test solution containing 10 to 100 μg of Pd(II) is mixed with 4 ml of DMF, 2 ml of a 0.1% solution of the reagent in DMF and 0.4 ml of 9M H_2SO_4 . The solution is diluted to 10 ml and the absorbance is measured against a reagent blank. Beer's law is obeyed for 1 to 10 ppm of Pd(II). The method has been used to determine Pd in catalysts. Copper (II) has also been determined with this reagent. The test solution containing 10 to 70 μg of Cu(II) is mixed with 4 ml of DMF, 2 ml of a 0.01% solution of the reagent in DMF and 1 ml of 4M H_2SO_4 . The solution is diluted to 10 ml, and after 15 min., the absorbance is measured at 487 nm against a reagent blank. Beer's law is obeyed for 0.2 to 8 ppm of Cu(II).	293
Benzyltriethylammonium ion and iodide in presence of EDTA	360 nm	5.0	Simultaneous extractive determination of palladium(II) and platinum(II), or palladium(II) and gold(III), with benzyltriethylammonium ion and iodide in the presence of EDTA is described. The sample solution	294

containing up to 100 μg of Pd(II) , 120 μg of Au(III) or 300 μg of Pt(II) is mixed with 1 ml of 1M EDTA, 1 ml of 1M benzyltriethylammonium ion, 1 ml of 1M I^- , acetic acid-aq. NH_3 buffer (pH 5) and 20 ml of isobutylmethyl ketone. After shaking for 3 min., the absorbance of the organic phase is measured at 360 nm for Pd(II) and at 370 nm for Au(III) and Pt(II) . for the simultaneous determination of Pd(II) - Pt(II) or Pd(II) - Au(III) , the above procedure is followed, except that the absorbance is measured at 550 nm for Pd(II) and at 370 nm for Au(III) or Pt(II) . The absorbance of Pt(II) and Au(III) complexes at 370 nm is then calculated by subtracting the absorbance of the Pd(II) complex at that wave length. Determination of 0.15 to 5 or 0.6 to 18 ppm of Pd(II) is achieved at 360 or 550 nm, respectively and of 0.5 to 15 ppm of Pt(II) and 0.2 to 6 ppm of Au(III) at 370 nm. The method is applied to determine Pd(II) - Pt(II) and Pd(II) - Au(III) in the presence of several other cations and is specific for the cited ions. Sulphide, CN^- and SCN^- did not interfere.

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
i) Phenyl-Hydrazodi- benzoyl methane (PHDBM) (I)	520 nm $\epsilon=1300$	3.0-3.5	The reagents(II) and (III) form reddish and greenish 1:2 (Pd:R) complexes whereas reagents (I) and (IV) form brownish and greenish 1:1 complexes with Pd(II). The absorbance is measured at the respective given wave lengths. Beer's law is obeyed for 0.023 to 0.740, 0.150 to 0.450, 0.025 to 0.850 and 0.025 to 0.580 $\mu\text{g/ml}$ of Pd with (I), (II), (III) and (IV) respectively. The correspond- ing solid complexes have been isolated and their UV, visible, I.R. and NMR studies reported. The pKa values of the ligands and stability constant of the complexes have also been reported.	295
ii) 2-Methyl-PHDBM (II)	530 nm $\epsilon=2300$	3.0-3.5		
iii) 3-Methyl-PHDBM (III)	560 nm $\epsilon=1000$	3.0-3.5		
iv) 4-Methyl-phenyl hydrazodibenzoyl methane (IV)	540 nm $\epsilon=1530$	3.0-3.5		

Name of the Reagent	λ max. or working wavelength with ϵ	pH	Remarks	Refs.
NN-Dimethyl-4-nitrosoaniline	495 nm $\epsilon=17,000$	4.6	An aq. solution containing 5 to 20 μg of Pd is treated with 1 ml of 0.02% reagent in ethanol and 10 ml of sodium acetate buffer (pH 4.6). This is diluted to 25 ml and absorbance is measured against a reagent blank. Beer's law is obeyed in the range 0.1 to 1.0 ppm of Pd in the final solution. Sandell's sensitivity is 1.4 ng/cm^2. Silver and EDTA interfere at all conc., as also do Br^-, I^- and SCN^-. Only small amounts of Pt(IV), Hg(II) and Rh(III) can be tolerated; a 100-fold excess of Cr, Co or Ni can be tolerated only by determination in 2M HCl medium, but with lower sensitivity. In the determination of 11.75 μg of Pd ($n=6$) results are $11.9 \pm 0.30 \mu\text{g}$.	296

Name of the Reagent	λ_{max} or working wavelength with ϵ	pH	Remarks	Refs.
Diphenylthiovaluric acid	425 nm	1.0-3.5	To an aliquot of solution containing 7-35 μg of Pt, a tenfold molar excess of the reagent in acetone is added and the pH is adjusted with sodium acetate and hydrochloric acid. The volume of the solution is raised to approximately 10 ml with water and then heated on a water-bath to evaporate acetone. The solution is then cooled and chloroform (10 ml) is added and shaken for 5 min. The separated chloroform layer is centrifuged to remove water droplets. The reagent forms a 1:2 (Pd:R) complex with Pd(II) and the absorbance is measured against a reagent blank. Beer's law is obeyed up to 4.96 ppm of Pd. Sandell's sensitivity is 0.0035 μg Pd/cm ² . In the determination of 3.5 ppm of Pd(II) the tolerance limits (ppm) of various cations and anions are as follows: bromide (250), borate (100), citrate, tartrate, nitrate, pyrophosphate or phosphate (2000), nitrite (1200), oxalate (250), Ca(II), Ba(II) or Sr(II) (1000), Pb(II) (100), Sn(II) (10), Sb(III) (100).	297

Mg(II) (500), Cd(II) (1000), Al(III) (100), Ag(I) (20), Bi(III) or As(III) (100), Se(IV) (20), Te(IV) (40), Ti(II) (100), Hg(II) (10), Ce(III) (20), W(VI) (500), V(V) (250), Be(II) (1000), Ga(III) or La(III) (200), Th(IV) (500), U(IV) or Mn(II) (1000), Zn(II) (1500), Cu(II) (150), Ni(II) or Co(II) (200), Fe(II) (20), Fe(III) (120), Au(III) (2), Rh(III), (20), Ru(III) (20, cit) Os(VIII) or Ir(III) (20) and Pt(IV) (10). Iodide, fluoride and thiosulphate interfere.

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