Original Paper

Enrichment and flame atomic absorption spectrometric determination of palladium using chelating matrices designed by functionalizing Amberlite XAD-2/16 and silica gel

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Abstract. Six chelating matrices have been prepared by anchoring 2,3-dihydroxypyridine (DHP) and 2-{[1-(3,4-dihydroxyphenyl)methylidene]amino}benzoic acid (DMABA) onto Amberlite XAD-2 and XAD-16 and 3,4-dihydroxybenzaldehyde (DHB), and iminodiacetic acid (IDA) onto silica gel. The materials were explored for enrichment of palladium followed by its determination with flame AAS. The optimum pH ranges for quantitative solid phase extraction by these matrices are from 4.0–5.5 to 5.5–7.0. The flow rates (column procedure) and concentration of HCl required for desorption have been optimized. Thiourea (~3%) is essential for quantitative recovery of Pd. The $t_{1/2}$ values are between 5 and 15 min. The sorption capacity varies from 38 to 192 $\mu mol\,g^{-1}$ (highest for silica gel loaded with iminodiacetic acid). The preconcentration factors were found in the range 20–150. Tolerance limits of foreign species in the enrichment are reported. The enrichment procedures coupled with FAAS determinations were applied to synthetic solutions corresponding to standards GBW07293 and NIST SRM 2557 successfully.

Key words: Amberlite; palladium; chelating matrix; solid phase extraction; flame atomic absorption spectrometry.

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The preconcentration/separation steps improve the detection limit and selectively of determination by flame atomic absorption spectrometry (FAAS). Several methods are known for preconcentration and separation of metal ions at trace/micro level and used according to nature of the sample, concentration of the analyte and measurement technique employed [1]. Ion exchange [2], co-precipitation [3–6], solvent extraction [7] and solid phase extraction (SPE) [8–21] are important among them but SPE with chelating matrices has rapidly grown in the recent past and coupled with FAAS and ICP-AES it is frequently used. The use of SPE in palladium enrichment and determination has also been reviewed in 1998 [22, 23]. There is growing concern [24] about the effect of Pd on human health because of its increasing occurrence in the environment as a result of its extensive use in automotive catalytic converters. This has made the development of reliable methodologies for Pd enrichment and determination in complex environmental and biological samples a subject of current importance. Several SPE based enrichment and determination methods have been developed for palladium in the recent past [25–32]. We have developed several chelating matrices in the last decade for enrichment of common metal ions [13–16, 19, 20]. It was therefore thought worthwhile to examine the following for

enrichment of palladium(II) followed by its estimation by flame atomic absorption spectrometry (FAAS).

(i) Amberlite XAD-2 and XAD-16 anchored with 2,3-dihydroxypyridine (DHP) (**I** and **II**)

(ii) Amberlite XAD-2 and XAD-16 anchored with 2-{[1-(3,4-dihydroxyphenyl)-methylidene]amino}-benzoic acid (DMABA) (**III** and **IV**)

(iii) Silica gel anchored with 3,4-dihydroxybenzaldehyde (DHB) and iminodiacetic acid (IDA) (**V** and **VI**)

The results of these investigations are reported in the present paper. Amberlite XAD-16 loaded with DMABA (AXAD-16-DMBA) and Amberlite XAD-2 loaded with 2,3-dihydroxypyridine (AXAD-2-DHP) have been found promising for preconcentration [33, 34] of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II) earlier.

Experimental

Instruments

A flame atomic absorption spectrometer (FAAS) of the Perkin-Elmer Instruments, Shelton, USA (www.perkinelmer.com; las.perkinelmer.com), model A analyst 100 equipped with air-acetylene flame (flow rate: air 8 and acetylene $4 \, L \, min^{-1}$) and hollow cathode lamp of Pd (current 30 A) was used for Pd determination. The wavelength used for its monitoring was 244.8 nm (slit width 0.2 mm). A Nicolet (Madison, USA; www.thermo.com/spectroscopy) FT-IR spectrometer, model Protégé 460, was used to record IR spectra (in KBr) in the range $400–4000 \, cm^{-1}$. The pH was measured with a digital pH meter (Toshniwal Instruments, Ajmer, India). Thermogravimetric analysis (TGA) was carried out on a Dupont (Wilmington, Delaware, USA) 2100 thermal analyzer and Perkin-Elmer (Rotkreuz, Switzerland; www.perkinelmer.com) elemental analyzer, model 240C, was used for elemental analyses. The cross polarization magic angle spinning (CPMAS) ^{13}C NMR spectrum was recorded at 75.3 MHz on a Bruker (Fallenden, Switzerland; www.bruker-biospin.com) 300 spectrometer. The flow of solution through the column was controlled using peristaltic pump (Watson-Marlow Model 101/U/R, Falmouth, UK; www.watson-marlow.com). The sorption and desorption studies of the metal on the chelating matrix were generally carried out on columns of 1 cm diameter (Pharmacia, Bromma, Sweden; www.pharmacia.com) and 10 cm in length equipped with adjustable frits. A mechanical shaker equipped with an incubator (Hindustan Scientific, New Delhi, India) with a speed of 200 strokes min^{-1} was used for batch equilibration.

Reagents

Amberlite XAD-16 (non-ionic divinyl polystyrene; specific area $800 \, m^2 \, g^{-1}$ and bead size, 20–60 mesh), Amberlite XAD-2 non-ionic divinyl polystyrene; specific area $330 \, m^2 \, g^{-1}$ and bead size, 20–60 mesh), Na_2PdCl_4 and 2,3-dihydroxypyridine (DHP) were procured from Aldrich (Milwaukee, USA; www.sigmaaldrich.com). 3,4-Dihydroxybenzaldehyde obtained from ACROS ORGANICS

(New Jersey, USA; www.acros.be) and anthranilic acid obtained from Merck India Ltd were used as received. The stock solutions of palladium(II) $(1000 \, mg \, L^{-1})$ was prepared by dissolving Na_2PdCl_4 in doubly distilled water acidified with dilute HCl. The solution was standardized by Flame AAS calibrated with standard solution of Pd(II) procured from Aldrich (Milwaukee, USA; www.sigmaaldrich.com). The $0.1 \, mol \, L^{-1}$ HCl and NaOH, $0.1 \, mol \, L^{-1}$ acetic acid-acetate buffer (pH 4 and 5), $0.1 \, mol \, L^{-1}$ phosphate buffer (pH 6 and 7) and $0.1 \, mol \, L^{-1}$ ammonia-ammonium chloride buffer (pH 8 and 9) were used to adjust the pH of the solutions, wherever suitable. The glassware were washed with chromic acid and soaked in 5% HNO_3 overnight and cleaned with doubly distilled water before use.

Synthesis of chelating matrices

Amberlite XAD-2 anchored with 2,3-dihydroxypyridine (DHP) [AXAD-2-DHP, **I**] was prepared by the published method [33]. On Amberlite XAD-16 also DHP was loaded by using identical experimental protocols to get AXAD-16-DHP (**II**). 2-{[1-(3,4-Dihydroxyphenyl)-methylidene]amino}benzoic acid (DMABA) was anchored on Amberlite XAD-16 to prepare AXAD-16-DMABA (**III**) by the procedure already published [34]. DMABA was grafted on Amberlite XAD-2 by using an identical procedure to obtain AXAD-2-DMABA (**IV**). For anchoring of 3,4-dihydroxybenzaldehyde (DHB) onto silica gel the published procedure [35] was used. For preparing IDA loaded silica gel the procedure used was as follows:

Activated silica gel (30 g) was suspended in 100 mL solution (15% v/v) of 2-(chloropropyl)triethoxysilane made in dry *p*-xylene. The mixture was refluxed with stirring for 72 h in N_2 atmosphere. The slurry was filtered and the resulting solid chloropropyl silica gel (CPSG) was washed with *p*-xylene, ethanol and diethylether (25–30 mL each) successively. It was dried and degassed at 373 K under vacuum for 6 h.

The chloropropyl silica gel (CPSG) (1.4 g) was mixed with iminodacetic acid (IDA) (4 g, ~3 mmol) in *p*-xylene (30–40 mL) and refluxed under N_2 atmosphere. The solid silica gel-IDA was filtered, washed with *p*-xylene, ethanol and diethylether (10–15 mL each) successively, dried and degassed at 375 K under vacuum for 6 h. Elemental analyses, ^{13}C CPMAS NMR, IR and TGA data of all the six chelating matrices are given below:

AXAD-2-DHP (**I**): Analyses: Found: C, 61.60, H, 4.84, N, 15.70%; NMR (^{13}C CPMAS), δ (ppm) 27.0–52.0 (aliphatic C), 108.0–130.0 (Ar–C), 148.0–152.0 (C–OH); IR (cm^{-1}): 1271 (C–O), 1448 (N=N), 1653 (C=N); TGA: 6.97% wt loss upto 150°C.

AXAD-16-DHP (**II**): Analyses: Found: C, 63.50, H, 4.31, N, 16.30%; NMR (^{13}C CPMAS), δ (ppm) 25.0–50.0 (aliphatic C), 100.0–132.0 (Ar–C), 140.0–150.0 (C–OH); IR (cm^{-1}): 1262 (C–O), 1500 (N=N), 1557, 1521 (phenyl), 1323 (O–H); TGA: 13.65% wt loss upto 150°C.

AXAD-2-DMABA (**III**): Analyses: Found: C, 59.30, H, 4.93, N, 9.44% NMR (^{13}C CPMAS), δ (ppm): 28.0–48.0 (aliphatic C), 109.0–132.0 (Ar–C), 148.0–150.0 (C–OH), 155.8 (C=N, C=O); IR (cm^{-1}): 1691(C=O), 1617(C=N), 1559 (N=N), 1343 (O–H), 1255 (C–O); TGA: 15.17% wt loss at 200°C.

AXAD-16-DMABA (**IV**): Analyses: Found: C, 62.73, H, 5.56, N, 9.90%; NMR (^{13}C CPMAS), δ (ppm): 24.0–47.0 (aliphatic C), 112.0–130.0 (Ar–C), 140.0–154.0 (C–OH), 158.8 (C=N, C=O) IR (cm^{-1}): 1686 (C=O), 1616 (C=N) 1569 (N=N), 1346 (O–H), 1243 (C–O) TGA: 9.20% wt loss at 200°C.

Silica gel-DHB (**V**): Analyses: Found: C, 15.23, H, 2.16, N, 1.89% NMR (^{13}C CPMAS), δ (ppm): 13.6 (Si–CH₂), 25.9 (CH₂), 45.9 (N–

Table 1. Optimum condition for enrichment of Pd

Matrix	pH	Optimum concn. range for Pd ($\mu g\,mL^{-1}$)		Flow rate: sorption (desorption) ($mL\,min^{-1}$)	Concentration of HCl + ~3% thiourea for desorption ($mol\,L^{-1}$)	Average recovery (RSD) (%)
		Column	Batch			
I	5.0–7.0	0.008–1.0	0.1–25.8	1.0–4.0 (2.0–4.0)	1.0	96.3 (3.32)
II	5.5–7.0	0.005–1.0	0.1–32.5	1.0–5.0 (2.0–5.0)	1.0	96.0 (3.53)
III	4.5–6.0	0.005–1.0	0.1–18.6	1.0–3.0 (2.0–5.0)	0.6	97.5 (3.26)
IV	4.0–6.0	0.004–1.0	0.1–26.5	1.0–5.0 (2.0–6.0)	0.6	98.4 (2.86)
V	4.5–6.0	0.004–1.0	0.2–22.1	1.5–3.0 (2.0–5.0)	2.0	97.0 (3.17)
VI	4.0–5.5	0.001–1.0	0.2–20.4	1.0–4.0 (2.0–5.0)	0.1	99.2 (2.82)

CH_2), 98.1, 111.3, 112.1, 117.9, 127.7 (Ar–C), 150.7 (C=N), IR (cm^{-1}): 1652 (C=N), 1471, 1506, 15058, 1598 (phenyl). TGA: 5.40% wt loss at 200 °C.

Silica gel-IDA (**VI**): Analyses: Found: C, 12.32, H, 2.65, N, 2.03%; NMR (^{13}C CPMAS), δ (ppm): 10.0 (Si–CH_2), 22.7 (CH_2 of IDA), 26.4 (CH_2), 49.3 (Cl–CH_2), 173.6 (CO), IR (cm^{-1}): 1710 (C=O), 2852, 2970 (C–H), TGA: 8.45% wt. loss at 220 °C.

Recommended column procedure for enrichment and determination

Chelating resin (1.0 g) was packed in a glass column C10/10 (Pharmacia, 10 cm × 10 mm), between frits, using the method recommended by the manufacturer [20] (Amberlite based matrices were swollen in water for 24 h before packing). The column was treated with 50 mL of HCl or HNO_3 (4 M for Amberlite based matrices and 2 M for silica gel ones) and washed with doubly distilled water until free from acid. A suitable aliquot of the sample solution containing Pd in the optimum concentration range given in Table 1 was passed through the column after adjusting its pH to the optimum value (Table 1) at a flow rate given in Table 1 and controlled with a peristaltic pump. The column was washed with distilled water to remove free metal ions. The bound metal ions were stripped from the column with 10–25 mL of HCl of suitable concentration (Table 1) containing 3% thiourea passed at an optimum flow (Table 1). The concentration of the metal ion in the eluates was determined by FAAS, standardized previously. Dilution with double distilled water was performed before aspiration when the eluates were sufficiently concentrated to exceed the working range of FAAS.

Recommended batch procedure for enrichment and determination

A sample solution (100 mL) containing 0.1–25.8, 0.1–32.5, 0.1–18.6, 0.1–26.5, 0.2–22.1, 0.2–20.4 $\mu g\,mL^{-1}$ of Pd for matrix **I–VI** respectively, was placed in a glass stoppered bottle (250 mL) after adjusting its pH to the optimum value (Table 1). One of the matrices **I–VI** (0.1 g) was added it. The bottle was stoppered and shaken for 30 min. The matrix was filtered and the metal ions from it were desorbed by shaking with 25 mL HCl or HNO_3 of optimum concentration (Table 1). The matrix was filtered off and the filtrate was aspirated into the flame of pre-standardized FAAS, after suitable dilution, if required.

Results and discussion

The chelating functionalities of **I–V** are shown in Scheme 1 along with reactions which result in **VI**.

IR data and ^{13}CP MAS NMR data authenticate the anchoring of ligands on Amberlite XAD-2/16 and silica gel surfaces. The weight losses in TGA up to 200 °C suggest the presence of one water molecule in **I**, two in **II**, **IV** and **V**, three in **VI** and four in **III**.

Optimum conditions for sorption and desorption

The multivariate approach was used to optimize sorption of Pd(II) on the columns packed with chelating matrices **I–VI**. Each optimum condition was established by varying one of them and following the recommended column procedure. It was rechecked after standardizing the remaining ones. A typical process for optimization of pH is as follow. A set of solutions (volume: 100 mL), containing 0.25 $\mu g\,mL^{-1}$ of Pd was taken. The pH of the solutions of the set was adjusted to different values in the range 2.0–9.0. The enrichment of palladium from these solutions was studied by the recommended column procedure. The optimum pH ranges for maximum recovery (96.0–99.2%) are 5.0–7.0, 5.5–7.0, 4.0–6.0 and 5.5.5 respectively for **I**, **II**, **III–V** and **VI**. The effect of pH on sorption was also studied by using the recommended batch method and the results are found to be consistent with those of the column method. The use of 5–10 mL of acetate, phosphate and ammonia buffer to adjust the pH does not affect the sorption behavior. The palladium is not significantly desorbed (<2%) by distilled water; therefore chelation contributes predominantly to its retention. The average recoveries under optimum conditions are in the range 96.2–99.2%. For five determinations of 0.25 $\mu g\,mL^{-1}$ of metal ion under optimum conditions the RSD was found to be 2.86–3.53%.

The Pd(II) sorption on columns packed with **I–VI** was studied at various flow rates controlled with a peristaltic pump. The results are given in Table 1. A flow rate <1.0 mL min^{-1} was not employed to avoid
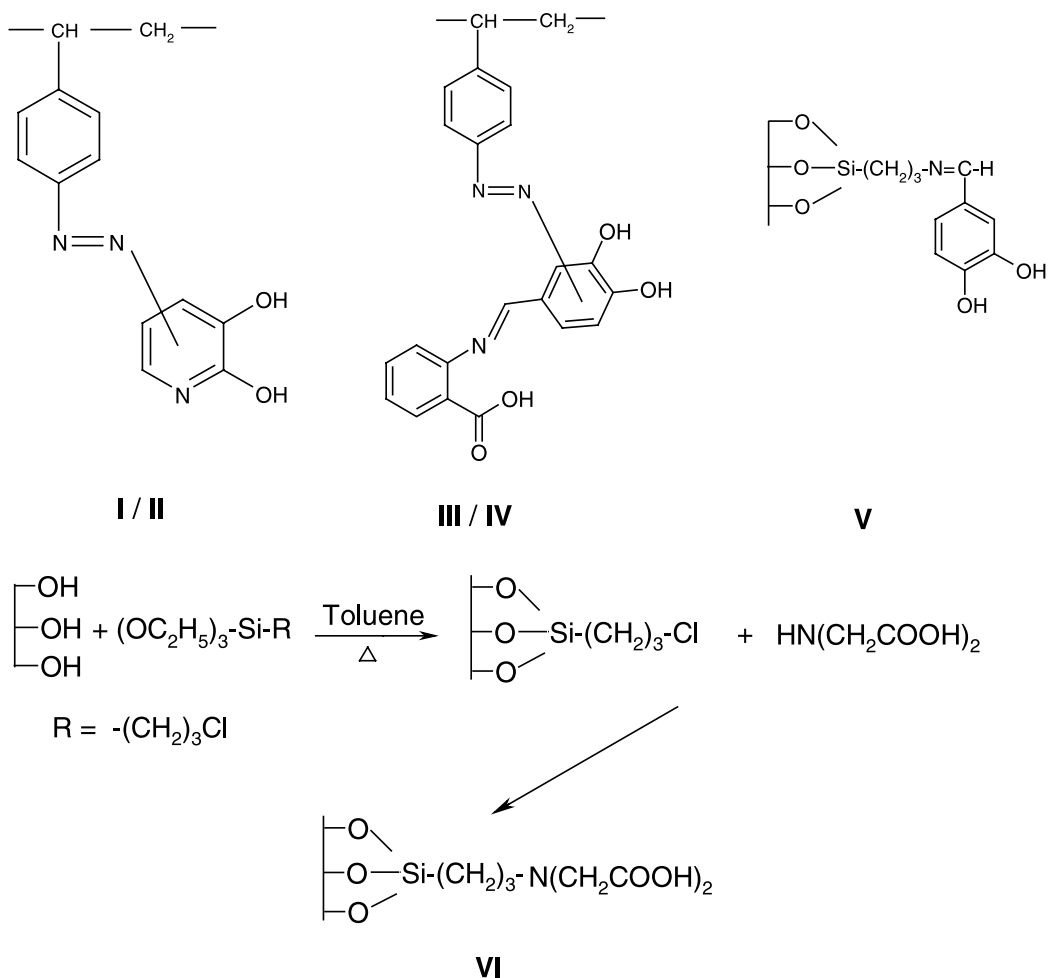
Scheme 1

the longer time of analysis. The decrease in the percentage of sorption at flow rate $>5.0/6.0\,mL\,min^{-1}$, is probably because the Pd(II) ions do not equilibrate sufficiently with the matrix. For stripping off bound Pd(II) the optimum concentrations of HCl (maximum instant recovery $>96.0\%$) needed are given in Table 1. The optimum flow rate for desorption have been found to be in the ranges 2.0–4.0 to 2.0–6.0 mL min^{-1}. Addition of thiourea ($\sim3\%$ w/v) was essential for quantitative recovery of Pd. In its absence recovery dropped very significantly (>20–30%).

Kinetics of metal sorption

The kinetics of sorption was studied by batch method. **I–VI** (0.5 g) was shaken with 50 mL of solution containing $40\,\mu g\,mL^{-1}$ of palladium(II) (2, 5, 10, 15, 20, 25, 30, 40 min and 5 h) under optimum conditions. The concentration of metal ions sorbed on the matrix

as well as present in the supernatant solution was determined with FAAS using recommended batch method for the former. The $t_{1/2}$ values are given in Table 1. The sorption is much faster on silica gel based matrices **V** and **VI**. Generally on organic polymer based matrices it has been found faster than those of silica gel ones [11].

Effects of electrolytes and cations

The effects of NaCl, NaBr, NaNO$_3$, Na$_2$SO$_4$, Na$_3$PO$_4$, NaI and other foreign species on the sorption of Pd (25 μg) onto **I–VI** were studied using the recommended column method. The tolerance limits of some foreign species in the sorption of palladium are given in Table 2. The 3d transition metal ions and other platinum metals are tolerable in 10 to 15-fold excess. The tolerance limits for individual species are recorded in Table 2. The criterion for interference was

Table 2. Tolerance limits of foreign species

Species	Matrix					
	AXAD-2-DHP	AXAD-16-DHP	AXAD-2-DMABA	AXAD-16-DMABA	Silica gel-DHB	Silica gel-IDA
NaNO$_3$[a]	0.30	0.35	0.34	0.40	0.32	0.45
NaCl[a]	0.40	0.44	0.50	0.55	0.20	0.67
NaBr[a]	0.12	0.16	0.22	0.26	0.12	0.22
Na$_3$PO$_4$[a]	0.08	0.11	0.12	0.16	0.08	0.18
Na$_2$SO$_4$[a]	0.44	0.50	0.52	0.56	0.38	0.58
NaI[a]	0.04	0.08	0.10	0.18	0.04	0.12
Humic acid[b]	6.0	8.0	10.0	12.0	6.0	15.0
Fulvic acid[b]	8.0	9.0	10.0	13.0	7.0	14.0
Ascorbic acid[c]	0.47	0.55	0.40	0.42	0.36	0.65
Citric acid[c]	0.18	0.20	0.14	0.20	0.18	0.25
EDTA[c]	0.002	0.003	0.001	0.002	0.001	0.014
Tartaric acid[c]	0.53	0.60	0.64	0.87	0.20	0.75
Oxalate[c]	0.70	0.68	0.71	0.83	0.34	0.87
Benzoate[c]	0.63	0.60	0.84	0.77	0.45	0.75
Phthalate[c]	0.50	0.58	0.61	0.63	0.24	0.77
Lactate[c]	0.28	0.20	0.24	0.20	0.38	0.25
Ethylene diamine[c]	0.18	0.10	0.14	0.10	0.18	0.15
Phenol[c]	0.48	0.30	0.34	0.40	0.28	0.35
Thiophenol[c]	0.18	0.10	0.14	0.10	0.18	0.25
Aniline[c]	0.38	0.30	0.34	0.30	0.28	0.34
2-Amino phenol[c]	0.11	0.10	0.14	0.10	0.12	0.13
Ca(II)[a]	0.16	0.20	0.23	0.20	0.14	0.24
Mg(II)[a]	0.28	0.22	0.32	0.38	0.19	0.30
Fe(III)[b]	36	37	38	37	30	32
Co(II)[b]	37	37	37	34	33	35
Ni(II)[b]	38	35	33	36	30	34
Pb(II)[c]	0.40	0.39	0.36	0.43	0.38	0.32
Mn(II)[b]	45	41	40	43	41	39
Cr(III)[b]	32	34	30	36	30	36
V(V)[b]	40	45	41	41	39	36
Ru(III)[b]	25	22	24	23	25	21
Pt(IV)[b]	24	22	25	24	28	25
Rh(III)[b]	29	28	27	28	22	25
Ir(III)[b]	26	24	29	26	27	22

[a] $= M$, [b] $= \mu g\,mL^{-1}$, [c] $= mM$.

lowering of recovery by more than 3%. Each reported tolerance/interference is in the preconcentration and not in the determination by FAAS, as checked with the help of reagent matched standard solutions. Tolerance of organic complexing agents is moderate only. It is apparent from the perusal of Table 3 that with Pd very excessive amounts of 3d transition metals and other platinum metals are not tolerable. These metals are also retained partly/or fully by the solid sorbers but by taking suitably larger amount of sorbent (depending on the total metal ion load in the solution) the situation can be handled without much difficulty.

Sorption capacity

The sorption capacities of chelating matrices **I–VI** for palladium(II) were determined by batch method. The matrix (0.1 g) was saturated with a Pd(II) solution (concentration: $50\,\mu g\,mL^{-1}$) by equilibration on a mechanical shaker under optimum conditions. The solid matrix was filtered, washed with distilled water and subjected to recommended batch procedure. The filtrate was diluted suitably and also subjected to FAAS determination. The results are given in Table 3. The sorption capacity values determined by column method were consistent with the batch method values (variation <1.2%). The **IV** and **VI** show most promising sorption capacity values.

Preconcentration and recovery of metal ions

Enrichment factors for column method were determined by increasing the dilution of palladium(II) solution while keeping the total amount of loaded Pd

Table 3. Sorption capacity and preconcentration parameters

Matrix	$t_{1/2}$ (min)	Sorption capacity (μmol g^{-1})	Total volume (final volume) (mL)	Concentration (ng mL^{-1})	Recovery (%)	Preconcentration factor
I	15	77.0	500 (15)	20	97.6	34
II	15	97.0	1000 (10)	10	97.4	100
III	10	95.0	750 (15)	27	98.2	50
IV	10	140.0	1000 (10)	20	99.1	100
V	5	38.0	500 (25)	50	96.0	20
VI	5	192.0	1500 (10)	10	98.7	150

Table 4. Analysis of standards for palladium content

Sample	Pd/μg g^{-1} (RSD/%)					
	I	II	III	IV	V	VI
GBW07293*	0.0418 (4.3)	0.0425 (5.9)	0.0432 (5.7)	0.0427 (5.3)	0.0437 (4.3)	0.0446 (4.9)
NIST SRM 2557**	231.6 (6.4)	232.3 (5.2)	232.4 (8.7)	231.9 (7.4)	231.8 (6.9)	232.6 (6.5)

* Metal content (μg g^{-1}): Pt, 0.0570; Pd, 0.0440; Ru, 0.0130, Ir, 0.0290; Rh, 0.0220; Au, 0.0050.
** Metal content (μg g^{-1}): Pd, 233.2; Pt, 1131, Rh, 135; Pb, 13931.

fixed and applying the recommended column procedure. These were guided by middle concentration value of calibration curve of each metal ion, as it should be available in the final eluate so that error is least. The feed volume and preconcentration factors are given in Table 3. The recoveries reported in Table 3 are at the lowest concentrations. The limit of detection values (defined as (blank $+$ 3s) where s is standard deviation of the blank determination) for the FAAS determination of Pd are: 0.59, 0.53, 0.40, 0.90, 0.74 and 0.80 μg L^{-1}, respectively for **I–VI** and corresponding limit of quantification (blank $+$ 10s) values are 1.47, 1.41, 1.30, 1.73, 1.52 and 1.55 μg L^{-1}, respectively. These limits were established by using feed and eluent volumes as 1 L and 25 mL, respectively.

Applications of palladium enrichment and determination

The validity and accuracy of palladium enrichment and determination have been established by applying the recommended column procedure to determine palladium content in synthetic solutions corresponding to geological standard reference material GBW07293 (Institute of Geophysical and Geochemical Prospecting, Langfang, China) and auto catalyst NIST SRM 2557 (National institute of Standards and Technology, Gaithersburg, USA). The results given in Table 4 authenticate the suitability of all six chelating matrices for palladium enrichment and determination in real samples. However, after using digestions procedures with real sample, an acidic solution will result.

This would need adequate neutralization before applying the recommended procedure.

Conclusions

All chelating matrices **I–VI** are suitable for enrichment of palladium but **IV** and **VI** are most promising. The **II** also shows good preconcentration factor. Interferences are generally lowest in case of **VI**. The matrices **III–VI** have advantage that optimum pH for extraction is acidic. The enrichment is fastest with **V** and **VI**. Addition of thiourea to HCl is essential for stripping Pd from the columns packed with chelating matrices, otherwise recovery is not quantitative.

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