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# Solvent-Extraction Behavior of Cobalt(II), Nickel(II), Copper(II), and Palladium(II) with Tri-*n*-butylphosphate

Anil K. De[a]; Asit K. Sen[a]
[a] Department of Chemistry, Jadavpur University, Calcutta 32, India

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# Solvent-Extraction Behavior of Cobalt(II), Nickel(II), Copper(II), and Palladium(II) with Tri-*n*-butylphosphate

ANIL K. DE and ASIT K. SEN
DEPARTMENT OF CHEMISTRY, JADAVPUR UNIVERSITY, CALCUTTA 32, INDIA

## Summary

A systematic study of the extraction behavior of cobalt(II), nickel(II), copper(II), and palladium(II) with TBP from thiocyanate system in various ranges of acid concentrations has been performed. The thiocyanate medium leads to enhanced extractions in all these cases compared to those in the previously used chloride medium. For palladium, the chloride and nitrate systems have been critically examined. Sixty-two per cent extraction occurs from 4 *M* hydrochloric acid using 100% TBP in a single run and the extraction becomes quantitative (>99%) after four successive equilibrations. A simpler method has been proposed for rapid extraction of palladium(II) as the thiocyanate complex. Quantitative extraction occurs in the presence of 1.2% thiocyanate solution from 0.5 to 2 *M* hydrochloric acid (initial) up to pH 8.0. The extractable species of cobalt(II), nickel(II), copper(II), and palladium(II) from thiocyanate medium are probably similar and of the type $[M(CNS)_4]^{2-}$ $[K{\cdot}TBP{\cdot}3H_2O]_2^+$ (buffer solution) and $[M(CNS)_4]^{2-}$ $[H{\cdot}TBP{\cdot}3H_2O]_2^+$ (acid solution). A simple extraction scheme has been worked out for the separation of palladium(II) from iron(III), cobalt(II), nickel, manganese(II), copper(II), and platinum.

Tri-*n*-butylphosphate (TBP) has been used as an extractant for a large number of elements (*1*). The present paper reports on the systematic studies of the extraction behavior of cobalt(II), nickel(II), copper(II), and palladium(II) with TBP from thiocyanate systems in various ranges of acid concentrations. For palladium, the chloride and nitrate systems and all the factors relating to solvent extraction have been critically examined and the optimum conditions have been worked out. A simple extraction scheme has been proposed for the separation of palladium from its common associates—iron(III), cobalt(II), nickel, manganese(II), copper(II), and platinum.

From the data on the solvent extraction of cobalt(II), nickel(II), copper(II), and palladium(II) with TBP from hydrochloric acid (*2–11*), it follows that only partial extraction of the metals is possible in a single extraction. Nickel(II) is extracted in traces only. Similar results are found regarding the solvent-extraction behavior of cobalt(II), nickel(II), and copper(II) with TBP from hydrochloric acid solution (*12*). The iodide complex of palladium(II) is extracted with 15% TBP in hexane (*13*), but platinum is coextracted along with palladium. About 85% of cobalt(II) or nickel cupferrates (*14*) is extracted with TBP from 0.01 *M* hydrochloric acid solution. The extraction of the thiocyanate complexes of copper(II) (*15,16*) and palladium(II) (*17*) with TBP has been studied. In the case of cobalt(II), nickel, and copper(II), no data about distribution ratios are available; and in the case of palladium(II) only countercurrent extraction is reported, using about 10 equilibrium stages. The present method for quantitative extraction of palladium with TBP from thiocyanate medium is much simpler and more rapid. Furthermore, the suggested thiocyanate method for extraction of cobalt, nickel, and copper with TBP represents definite improvement over the earlier methods reported by previous workers.

## APPARATUS

Separatory funnels (250 ml) were used for extraction. All the pH measurements were carried out with a Cambridge pH meter. The chemicals used were either chemically pure or reagent-grade material unless otherwise mentioned.

### Reagents

*Tributyl phosphate.* This reagent (Matheson, Coleman, and Bell, Cincinnati, Ohio), b.p. 143 to 145° at 5 mm, was employed as extractant after purification according to the method of Peppard et al. (*18*), i.e., washing first with 8 *M* hydrochloric acid, then with 5% sodium carbonate, and finally with water.

*Palladium chloride solution* (5.43 mg of palladium per ml). About 4 g palladium chloride (Johnson, Matthey and Co., London) dissolved in 13 ml of concentrated hydrochloric acid and total volume of the solution was made up to 400 ml. The solution was standardized by the dimethylglyoxime method (*19*).

*Cobalt sulfate solution* (5.59 mg of cobalt per ml). About 11 g of cobaltous sulfate (E. Merck) was dissolved in 500 ml of water. The solution was standardized gravimetrically with α-nitroso-β-naphthol (*19*).

*Nickel sulfate solution* (5.52 mg of nickel per ml). About 12.5 g of nickel sulfate (Reidel-Haen) was dissolved in 500 ml of distilled water and the solution was standardized by the dimethylglyoxime method (*19*).

*Copper sulfate solution* (5.04 mg of copper per ml). About 10 g of copper sulfate pentahydrate was dissolved in 500 ml of water and 1 ml of concentrated sulfuric acid and the solution was standardized by the iodometric method (*19*).

Buffer solutions of different pH were prepared by standard procedures: pH 2 (chloroacetate); pH 3.3 (acetate–hydrochloric acid); pH 4 to 6 (acetate–acetic acid); and pH 8.0 (ammonia–ammonium chloride).

### General Procedure

A 2-ml aliquot of the test solution containing about 10 mg of the metal under investigation was mixed in a 250-ml separatory funnel with the requisite volume of hydrochloric acid or nitric acid to study the effect of acidity or with 13 ml of requisite buffer solution to study the effect of pH. In the experiments involving salting-out agents and diverse ions, the appropriate salting-out agents and foreign ions were added before introducing the acid. When the extraction of thiocyanate complexes was studied, 5 ml of potassium thiocyanate solution of desired concentration was added after introduction of the acid or buffer solution. The resultant aqueous phase in all cases was made 20 ml in volume and was extracted with 10 ml of 100% TBP for 5 minutes. In the case of metal extraction from an acid medium, the TBP was saturated with the appropriate acid before extraction. Where the effect of TBP concentration was studied, benzene was used as the diluent. At the end of the extraction, the two layers were allowed to separate. The aqueous phase was retained for measurement of acidity or pH and also for determination of any residual metal ion (in duplicate runs).

The metal ion was then stripped from the TBP layer by consecutive shaking for 5 minutes with 2 × 20 ml of 20% aqueous ammonia followed by 10 ml of 0.1 *M* hydrochloric acid. To remove any TBP entrained in the combined back-extracts, the latter was washed with 5 ml of benzene in a separatory funnel.

To remove the interference of the thiocyanate ion in the estimation of palladium by dimethylglyoxime, the back-extract was evaporated to a small volume with frequent addition of ammonia to keep the solution colorless (red color of palladium thiocyanate complex was discharged by adding ammonia, so that only cationic amino complex of palladium was present). This was then quickly passed through an anion exchanger (Dowex 21-K, 50–100 mesh column 1.0 cm × 18 cm). In the case of copper, some reduction of copper(II) was observed in the presence of potassium thiocyanate in an acid medium, so before estimation of copper, the solution should be oxidized by boiling in a nitric acid–sulfuric acid mixture. The solution after cooling was treated with urea to remove any nitrite.

Cobalt and nickel were estimated by complexometric titration with ethylenediamine tetraacetic acid (*20*), copper iodometrically (*19*), and palladium gravimetrically with dimethylglyoxime (*19*).

## RESULTS AND DISCUSSION

### Effect of Acidity or pH

The solvent-extraction behavior of the thiocyanate complex of

TABLE 1

Distribution Ratio of Thiocyanate Complexes as a Function of Acid Concentration (Metal:thiocyanate mole ratio = 1:25)

| HCl, *M* (initial) | $Ni^{2+}$ | $Cu^{2+}$ | $Co^{2+}$ | $Pd^{2+}$ |
|---|---|---|---|---|
| 6.9 | — | 0.95 | — | — |
| 6.0 | Extraction negligible | 0.99 | 0.19 | 19.7 |
| 4.0 | | 1.25 | — | — |
| 2.0 | | 1.32 | 0.23 | Complete extraction |
| 1.0 | | 8.01 | — | Complete extraction |
| 0.5 | | 10.23 | — | Complete extraction |

cobalt(II), nickel(II), copper(II), and palladium(II) with respect to TBP was investigated at varying concentrations of hydrochloric acid and over the pH range 1 to 8. The distribution ratio (*D*) was computed from the ratio of the metal ion concentrations in the organic and aqueous phases. The cobalt and nickel in both phases were determined by complexometric titration, the copper in both phases was determined by iodometric titration, and the palladium in the organic phase only was determined gravimetrically with dimethylglyoxime.

Table 1 shows that the extraction of all metals under investigation with 100% TBP decreases with increasing acid concentration. Presumably the lower acidities favor the formation of thiocyanate complexes, which lead to enhanced extraction. At higher acid concentration (>2 *M*), potassium thiocyanate becomes unstable and copper(II) is reduced to copper(I) and palladium(II) to metallic palladium. Cobalt(II) and nickel(II) remain unaffected. However, the extraction of nickel is negligible in the presence of acid and the extraction of palladium(II) becomes quantitative from 0.5 to 2.0 *M* hydrochloric acid. The *D* values for cobalt(II) and copper(II)

**TABLE 2**

Distribution Ratio of Thiocyanate Complexes as a Function of pH

| Initial acidity or pH | $Ni^{2+(a)}$ | $Cu^{2+(b)}$ | $Co^{2+(a)}$ | $Pd^{2+(c)}$ |
|---|---|---|---|---|
| 0.5 *M* HCl | 0.15 | 18.23 | — | Complete extraction |
| 0.2 *M* HCl | — | 30.05 | — | Complete extraction |
| 0.1 *M* HCl | 1.16 | Complete extraction | 91.18 | Complete extraction |
| pH 3.3 | 2.00 | Complete extraction | — | Complete extraction |
| pH 4.0 | — | Complete extraction | Complete extraction | Complete extraction |
| pH 6.3 | 2.10 | Complete extraction | Complete extraction | Complete extraction |
| pH 8.0 | 2.19 | — | Complete extraction | Complete extraction |

[a] $[CNS^-]$ in the aqueous phase is 6%.
[b] $[CNS^-]$ in the aqueous phase is 2%.
[c] $[CNS^-]$ in the aqueous phase is 1.15%.

from hydrochloric acid-thiocyanate medium are much higher at lower acidity than those reported by Irving et al. (2) [1 *M* HCl, $D = 0.0039$ (2); $D = 8.01$, our value for Cu(II)].

Table 2 shows that the extraction of all metals under investigation with 100% TBP (3.66 *M*) increases with increasing pH. The extraction of copper(II) becomes quantitative (>99%) from 0.1 *M* hydrochloric acid (initial) to pH 6.0 (initial) and the extraction of cobalt(II) becomes quantitative (>99%) from pH 4 to 8. However, the extraction of nickel(II) is not complete, and maximum extraction (52.6%) occurs at pH 6.0 to 8.0. It is interesting that palladium can be quantitatively extracted in a single extraction from 0.5 to 2 *M* hydrochloric acid (initial) down to pH 8 in the presence of thiocyanate (1.15%). Thus the thiocyanate medium is definitely better than the chloride medium, used by earlier workers, for the extraction of these metals. The recommended optimum pH ranges for extraction are: Co, pH 4 to 8; Ni, pH 6 to 8; Cu, pH 2 to 8; and Pd, pH 2 to 8.

The palladium(II)-TBP system has also been investigated from hydrochloric acid and nitric acid media. Table 3 shows that the extraction of palladium(II) increases with increasing acid concentration and becomes maximum, i.e., 61.8%, at 4 *M* (equilibrium acid, 4.10 *M*) hydrochloric acid and 44.38% at 0.5 *M* (equilibrium

**TABLE 3**

Distribution Ratio (Palladium) as a Function of Acid Concentration[a]

| HCl, *M* (initial) | Distribution ratio, *D* | $HNO_3$, *M* (initial) | Distribution ratio, *D* |
|---|---|---|---|
| 0.06 | 0.37 | 0.10 | 0.82 |
| 0.16 | 0.40 | 0.50 | 0.97 |
| 1.0 | 0.57 | 1.0 | 0.62 |
| 2.0 | 1.30 | 4.0 | No extraction |
| 3.0 | 1.49 | | |
| 3.5 | 1.85 | | |
| 4.0 | 1.95 | | |
| 5.0 | 1.67 | | |
| 6.0 | 1.46 | | |
| 8.0 | 1.01 | | |

[a] 10.86 mg of palladium.

value, 0.5 *M*) nitric acid and then decreases with increasing acid concentration. It should be mentioned here that the distribution ratio *D* for palladium at 4 *M* hydrochloric acid is 1.95, which is much higher than that obtained by Berg and Senn (*11*) (0.5 as obtained from the graph). At 4 *M* nitric acid palladium is not at all extracted. However, to study the other effects (i.e., salting-out agents, diverse ions, etc.) on the extraction of palladium(II) with TBP, the aqueous phase was made 4.0 *M* (equilibrium acidity 4.10 *M*) with respect to hydrochloric acid to keep the interferences of other ions at a minimum.

Quantitative extraction (>99%) of palladium from hydrochloric acid (4 *M*) can be achieved by extracting palladium four times with acid-saturated TBP (4 × 10 ml).

Addition of ammonium chloride (2 *M*), sodium chloride (2 *M*), and aluminium chloride (1 *M*) lowers the extraction, probably by masking action. These do not show any salting-out effect.

The optimum period of extraction is 5 minutes. Using different metal ion concentrations it has been found that under the optimum conditions, the suggested method can handle from 0.1 to 30 mg of the metal ion without any trouble at all. This indicates that at higher metal ion concentrations (10 to 30 mg) there is no danger of polymerization in the organic phase.

## Effect of Thiocyanate Concentration

An interesting observation was noted during the study of the effect of thiocyanate concentration on the solvent-extraction behavior of palladium(II) with TBP. Excess of thiocyanate (~15%) in the aqueous phase lowers the extraction. Palladium is completely extracted from both hydrochloric acid (0.5 to 2 *M*) solution and buffer solutions of different pH when the thiocyanate concentration in the aqueous phase is 1.15% (palladium : thiocyanate mole ratio is 1:25). At higher acid concentrations the thiocyanate is unstable and reduces palladium(II) to metallic palladium. This effect is also observed at lower acid concentrations when the thiocyanate concentration in the aqueous phase is increased. This difficulty can be overcome by extraction from the buffer solutions of different pH (up to 8.0).

In the case of cobalt and nickel at 6% thiocyanate concentration in the aqueous phase, the distribution ratio is maximum; but when the thiocyanate concentration is 2 and 15%, respectively, in the aqueous phase, the distribution ratio decreases somewhat.

In the case of copper, the distribution ratio increases with decreasing acidity and increasing pH, when the thiocyanate concentration in the aqueous phase is 2%. Complete extraction takes place from 0.1 *M* hydrochloric acid (initial) solution. No effect is found when the thiocyanate concentration in the aqueous phase

**TABLE 4**

Effect of Thiocyanate Concentration (%) on the Distribution Ratio

| Initial acidity or pH | $Ni^{2+}$, % | | | $Co^{2+}$, % | | | $Pd^{2+}$, % | | |
|---|---|---|---|---|---|---|---|---|---|
| | 2 | 6 | 15 | 2 | 6 | 15 | 2 | 6 | 15 |
| 0.1 *M* HCl | — | — | — | — | 91.18 | 30.12 | Complete extraction | — | 12.98 |
| pH 3.3 | 0.42 | 2.0 | 1.51 | — | — | — | Complete extraction | — | 21.11 |
| pH 4.0 | — | — | — | 6.68 | Complete extraction | Complete extraction | Complete extraction | — | 44.21 |
| pH 4.5 | — | — | — | — | — | — | Complete extraction | — | 169.6 |

**TABLE 5**

Distribution Ratio as a Function of TBP Concentration[a]

| TBP concentration, % | Distribution ratio, $D^b$ | Distribution ratio, $D^c$ | Distribution ratio, $D^d$ |
|---|---|---|---|
| 100 (3.66 *M*) | 1.95 | 1.30 | Complete extraction |
| 90 (3.294 *M*) | 1.48 | 0.57 | Complete extraction |
| 80 (2.93 *M*) | — | 0.18 | 33.02 |
| 75 (2.74 *M*) | 0.69 | — | — |
| 70 (2.56 *M*) | — | 0.07 | 5.36 |
| 60 (2.20 *M*) | 0.22 | — | — |
| 50 (1.83 *M*) | 0.15 | No extraction | 0.53 |

[a] 10.86 mg of palladium.

[b] Aqueous phase, 4 *M* HCl.

[c] Aqueous phase, 2 *M* HCl.

[d] Aqueous phase, acetate buffer (pH 6.1) + [KCNS], 2%.

increases to 15% at pH 4, but difficulty arises when the extraction takes place from hydrochloric acid solution. There is profuse liberation of sulfur with reduction of copper(II) to copper(I) at $\geq 1.0$ *M* hydrochloric acid solution containing 15% thiocyanate concentration (Table 4).

Thus the optimum thiocyanate concentrations are: 2% for Cu (pH 2 to 8); 6% for Ni (pH 6 to 8); 6% for Co (pH 4 to 8); 1.2–2% for Pd (pH 2 to 8).

### TBP Concentration

The concentration of TBP was varied from 50% (1.83 *M*) to 100% (3.66 *M*) with benzene as diluent (Table 5). The effect on the extraction was noted at two different acid concentrations and also at pH. Dilution of TBP lowers the extraction. Below TBP concentration of 50% experiments were not carried out, because the extraction is very poor and the accuracy of measurement unsatisfactory.

### Nature of the Complex

A few ion-exchange experiments were undertaken to explore the nature of the extracted species. When the organic phase after extraction of the system Co–KCNS–acetate buffer(pH 6)–TBP was passed through an anion-exchange resin (Dowex 21-K, 50–100 mesh) column (1.0 cm × 18 cm), the greenish-blue complex is completely adsorbed on the resin bed. After washing with water, the bed is washed with ammonium nitrate (20%) solution. The presence of cobalt and thiocyanate is detected in the effluent. This proves that an anionic complex of the type $Co(CNS)_4^{2-}$ is extracted with TBP. The extracted species is presumably of the type $[Co(CNS)_4]^{-2}$ $[K{\cdot}TBP{\cdot}3H_2O]_2^+$ when extracted from buffer solutions, and $[Co(CNS)_4]^{-2}$ $[H{\cdot}TBP{\cdot}3H_2O]_2^+$ when extracted from acid solutions (<2 *M* HCl). These are analogous to the solvated species $[H{\cdot}TBP{\cdot}3H_2O]_2^+$ $[CuCl_4]^{-2}$ as reported by Morris et al. (*10*). Similarly, after extraction of the system Co–KCNS–HCl(4 *M*)–TBP, the organic phase was passed through the resin bed and the greenish-blue complex was completely adsorbed, indicating the presence of mixed chloro- and thiocyanate complexes.

The same observations apply to copper and palladium.

## Diverse Ions

The extractions were carried out from 4 *M* hydrochloric acid (62% extraction in single run). Thiocyanate medium, which gives quantitative extraction, was avoided, owing to possible interferences of many ions.

Seventeen representative ions were carried through the procedure and examined for interference. The tolerance limit for each, recorded in Table 6, represents that concentration of the foreign ion in the presence of which palladium(II) can be extracted and then recovered within ± 2%. It is interesting to note that nickel(II) and manganese(II) (100 mg) are not extracted; cobalt(II), bismuth(III) (10 mg), and silver(I) (5 mg) are coextracted in traces, but during back-extraction with 20% aqueous ammonia, bismuth and silver were precipitated and hence removed by simple filtration. A trace amount of cobalt does not interfere during estimation of

**TABLE 6**

Effect of Diverse Ions[a]

| Foreign ion | Tolerance limit to ion, $\mu g$ |
|---|---|
| $Ni^{2+}$ ($NiSO_4$, $6H_2O$) | $10^5$ |
| $Mn^{2+}$ ($MnSO_4$, $5H_2O$) | $10^5$ |
| $W^{6+}$ ($Na_2WO_4$, $2H_2O$) | $1 \times 10^{4(b)}$ |
| $Bi^{3+}$ ($BiOCl$) | $1 \times 10^{4(c)}$ |
| $Co^{2+}$ ($CoSO_4$, $7H_2O$) | $1 \times 10^{4(d)}$ |
| $Ag^+$ ($AgNO_3$) | $5 \times 10^{3(c)}$ |
| $U^{6+}$ [$UO_2(NO_3)_2$, $6H_2O$] | $1 \times 10^{5(e)}$ |
| $Pt^{4+}$ ($H_2PtCl_6$) | $1.5 \times 10^{3(d)}$ |
| $Cu^{2+}$ ($CuSO_4$, $5H_2O$) | $1 \times 10^{3(d)}$ |
| $Fe^{3+}$ [$NH_4Fe(SO_4)_2$, $12H_2O$] | $1 \times 10^{3(d)}$ |
| $SO_4^{2-}$ ($Na_2SO_4$ anhyd.) | $5 \times 10^5$ |
| Tartrate (tartaric acid) | $1 \times 10^6$ |

[a] 10.86 mg of palladium; TBP = 100%; 4 *M* HCl.

[b] In the presence of tartaric acid.

[c] $Bi^{3+}$ and $Ag^+$ are coextracted in traces, but during back-extraction precipitated and are removed by filtration.

[d] $Pd^{2+}$ is extracted from 0.5 *M* $HNO_3$. $Fe^{3+}$ and $Co^{2+}$ are coextracted in traces, but they remain in the organic phase during back-extraction with 4 *M* $HNO_3$.

[e] $U^{6+}$ first extracted from 4 *M* $HNO_3$.

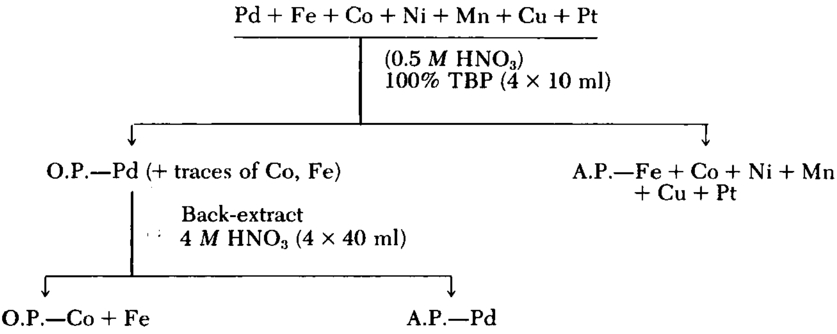
palladium. Uranium(VI), tungsten(VI), platinum(IV), copper(II), iron(III), vanadium(V), and molybdenum(VI) are coextracted. Uranium(VI) is removed first by extracting with 100% TBP from 4 *M* nitric acid. The metal in aqueous phase, after evaporating nearly to dryness and removing nitric acid with sulfuric acid, is extracted from 4.0 *M* (initial acid) hydrochloric acid. The interferences due to platinum(IV), copper(II), iron(III), and cobalt(II) can be similarly eliminated (see the next section). In the presence of tartaric acid, tungsten(VI) remains in the aqueous phase and thus coextraction is prevented.

Sulfate and tartrate do not interfere in the extraction. Fluoride and oxalate interfere in the extraction.

### Extraction Scheme for Separation of Palladium from Iron(III) Cobalt(II), Nickel(II), Manganese(II), Copper(II), and Platinum(IV)

To the solution of the mixture in a separatory funnel is added the requisite amount of nitric acid to give a strength of 0.5 *M* with respect to nitric acid. Then the mixture is extracted with 100% TBP (4 × 10 ml), previously saturated with 0.5 *M* nitric acid. Under this condition only palladium, together with slight traces of cobalt and

**Extraction Scheme**



O.P., organic phase, A.P., aqueous phase

| Taken, mg | Recovered, mg | Recovery of Pd, % |
|---|---|---|
| Pd, 10.86; Fe, 5; Co, 5; Ni, 5; Mn, 5; Cu, 5; Pt, 5 | Pd, 9.92, 9.95, 9.92 | 91.4, 91.6, 91.4 |

iron, is extracted. The combined organic phase is back-extracted with 4 *M* nitric acid (4 × 40 ml). At this stage the traces of iron and cobalt (coextracted with palladium) are left behind in the organic phase. The back-extract is washed with 15 ml of benzene to remove any dissolved TBP and then evaporated to a small volume (25 ml). Palladium is then estimated with dimethylglyoxime. With three runs the results show an average of 91.5% recovery of palladium from the synthetic mixture.

## Recommended Procedure for Palladium

*Extraction of palladium(II) as thiocyanate complex.* Take an aliquot of palladium(II) chloride (Pd, up to 30 mg) in a 250-ml separatory funnel, then add 10 ml of requisite buffer solution (pH 2 to 8) followed by 5 ml of potassium thiocyanate solution (mole ratio, Pd/SCN = 1/25). Make up the volume of the solution to 20 ml. Mix well and shake the resultant aqueous phase with 10 ml of 100% TBP for 5 minutes and allow the phases to separate. Proceed as described under general procedure.

*Extraction of palladium(II) as chloro complex.* Take an aliquot of palladium(II) chloride solution (Pd, up to 30 mg) in a 250-ml separatory funnel. Add 8 ml of 10 *M* hydrochloric acid plus distilled water, so that the final acid concentration becomes 4.0 *M* with respect to hydrochloric acid in a total volume of 20 ml. Shake the resultant aqueous phase with 10 ml of acid-saturated TBP for 5 minutes and allow the phases to separate. Proceed as described under general procedure. Sixty-two per cent extraction occurs in a single run. Four equilibrations are necessary for quantitative extraction.

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