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Extraction-Spectrophotometric Determination of Pd(II) with 4-(3,5-Dichloro-2-pyridylazo)-1,3-diaminobenzene and Trichloroacetate. II

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The influence of different variables affecting the extraction of Pd(II) with 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene (3,5-Cl2PADAB) and trichloroacetate are described. The complexation reaction between palladium(II) and 3,5-Cl2PADAB, in 1 M trichloroacetic acid aqueous solutions containing ethanol (10% v/v) and an acidity range from pH near 1 to 2 M H_2SO_4 is completed 10 min after having mixed the reagents. Under these experimental conditions, Pd(II) is extracted into benzene as an colored ion-association compound with trichloroacetate. At 600 nm, Beer's law is fulfilled up to a Pd(II) concentration of 2.16 ppm, being the most appropriate concentrations for the metal spectrometry those ranging from 0.24 to 2.12 ppm. The apparent molar absorptivity is 8.60×10^4 dm^3 mol^{-1} cm^{-1}, and the method's sensitivity (Sandell) of 0.00123 μg Pd(II)·cm^{-2}. The assayed procedures for suppressing the most serious interferences produced by Au(III) and Hg(II) are specified, and the procedure for increasing the tolerance as to Ag(I), Cu(II), Co(II), Cr(III)–(IV), Ir(III)–(IV), Os(VIII), and Ru(III)–(VIII) are described.

In previous papers[1,2] we showed that Pd(II) reacts with 4-(3,5-dichloro-2-pyridylazo)-1,3-diaminobenzene (3,5-Cl2PADAB=L) in an acidity range from pH 4 to 2 M† H_2SO_4 (or from pH 4 to 3 M $HClO_4$) to form three complexes having an equal metal-to-reagent molar ratio (1:1) though different Pd(II)-to-H^+ ratio.

These complexes were assigned as the formulas of $PdH_nL^{(2+n)+}$ ($n>1$), $PdHL^{3+}$, and PdL^{2+}. They are related to each other by means of reversible acid–base equilibria, and the formation of one species or another depends on the acidity of the reaction medium.

The complex species $PdHL^{3+}$ and PdL^{2+} are quantitatively extracted into benzene in the form of ion-association compounds formed with trichloroacetate (TCA^-) under different acidity conditions.[2] Pd(II) is extracted as $PdHL^{3+}\cdot(TCA^-)_3$ in the acidity range from pH near 1 to 2 M H_2SO_4, while in less acid aqueous ethanol phase (pH range 3—4) it is quantitatively extracted as $PdL^{2+}\cdot(TCA^-)_2$. The high molar absorptivity of the ion-association compound $PdHL^{3+}\cdot(TCA^-)_3$ dissolved in benzene, as well as its suitable solubility in this solvent, accounted for carrying-out a study focused on establishing the most appropriate experimental conditions for the separation and spectrophotometric determination of palladium(II).

This is the aim of this work, as well as to describe the procedures assayed in order to avoid the interference of some metallic ions, and eliminate or, at least, reduce to allowable values their concentrations in solutions containing together with Pd(II), in those particular cases in which they are found at higher proportions than the tolerated by the proposed procedure.

† 1 M=1 mol dm^{-3}.

Experimental

Apparatus. A Varian 634 UV model spectrophotometer was used for recording spectra and individual absorbance measurements, with 10-mm path-length glass or quartz cells. The pH was measured on an Orion pH-meter model 701 A, equipped with a glass/Ag–AgCl combination electrode.

Reagents. 3,5-Cl2PADAB Solutions: The reagent was synthesized as previously described.[1] Ethanol solution (0.025% (w/v) of the pure material was generally used. When necessary, other solutions with the required concentration were prepared either by diluting the previous solutions with the same solvent, or by direct weighing of the reagent.

5×10^{-3} M Pd(II) Solution: Distilled water (50 ml) and concentrated sulfuric acid (2 ml) were added to 0.2664 g of $Pd(NO_3)_2\cdot2H_2O$ contained in a 150 ml precipitation flask. The whole was softly heated until complete dissolution of the salt. Once cooled, the resulting solution was transferred to a 200 ml volumetric flask and then the volume made up to the mark with distilled water. The metal's actual concentration was complexometrically determined.[3] This solution, stored in a glass vessel, keeps its concentrations unchanged for 5 days. More diluted solutions of Pd(II) were daily prepared from the previous one.

Trichloroacetic Acid Standardized Solution: An approximately 5 M solution (500 cm^3) of the acid was prepared from the solid reagent. The exact content of trichloroacetic acid was alkalimetrically determined on portions of the previous solutions.[4] All other reagents used were of analytical grade.

General Procedures. The trichloroacetate anion was added in the aqueous phases as trichloroacetic acid standardized solution, and the 3,5-Cl2PADAB reagent as an ethanol solution. For the extraction, the solutions were mechanically shaken in 100 mm long.×35 mm diameter "Pyrex-type" glass tubes with polyethylene stoppers. The temperature was kept at 20±0.5 °C. The percentage of palladium(II) extracted was calculated by determining both the amount of metallic ion transferred to the organic phase and that remaining in the aqueous phase after the

equilibrium is reached, using a spectrophotometric procedure that employes 3,5-Cl2PADAB.[1] When dealing with the extraction of single ion-association compound, the %E was evaluated by means of the absorbance measurements of its organic extracts at the maximum absorption wavelength of the spectral curve of that compound. To do this, it was necessary to previously determine the value of its molar absorptivity under the experimental conditions of the quantitative extraction of Pd(II).

Recommended Procedure for the Extraction-Spectrophotometric Determination of Palladium(II). In an extraction tube, put 2 cm^3 of acid solution of the sample containing no more than 27 ppm of Pd(II), 5 cm^3 of 2 M HTCA solution, 0.5—1 cm^3 of 96% H_2SO_4, 1 cm^3 of 0.025% ethanol solution of the reagent, and make volume up to 10 cm^3 with distilled water. Let it stand for 15 minutes and then, add 10 cm^3 of pure benzene. Shake the whole mechanically during 15 minutes. Allow the phases to separe, and then decant the organic layer into a 25 cm^3 dry volumetric flask. Wash the aqueous phase twice with 3 cm^3 portion of pure benzene; mix the washing liquids together with the bulk of the organic extract and, afterwards dilute up to the mark with pure benzene. If the so-obtained solution shows any turbidity, centrifuge before carrying out the absorbance measurement at 600 nm against a reagent blank. Calculate the palladium concentration from a calibration curve obtained by operating in the same way.

Results and Discussion

Although 3,5-Cl2PADAB is soluble in benzene, no less than a 45 min agitation period was required for the quantitative extraction of Pd(II) when the reagent dissolved in benzene was used. This is because, on the one hand, the complexation reaction needs at least 10 min to become complete and, on the other, the reagent is only slightly transferred to the aqueous phase under the experimental conditions exacted for the quantitative extraction of the metallic ion. This latter fact contributes to reduce the rate of the complexation reaction in the aqueous phase. Thus, in order to reduce the time interval employed in the extraction, the reagent has to be added as the ethanol solution to the aqueous phase. Once the Pd(II)-3,5-Cl2PADAB complexation reaction is over, the complex formed can be extracted into benzene in a second stage.

For the extraction of Pd(II) with 3,5-Cl2PADAB and trichloroacetate other organic solvents immiscible with water, such as higher alcohols, esters, ethers, chloroform, carbon tetrachloride, etc., were tested, but benzene was selected due to the greater stability of the extracted solute dissolved in this solvent.

Influence of the Trichloroacetic Acid and Ethanol Concentrations. The extraction was studied up to 2 M HTCA concentration. Different minimum concentrations of the organic acid was required for extracting the PHL^{3+} mixed-complex and the excess of the reagent (Fig. 1). 1 M was the optimum concentration of HTCA which ensures complete extrac-

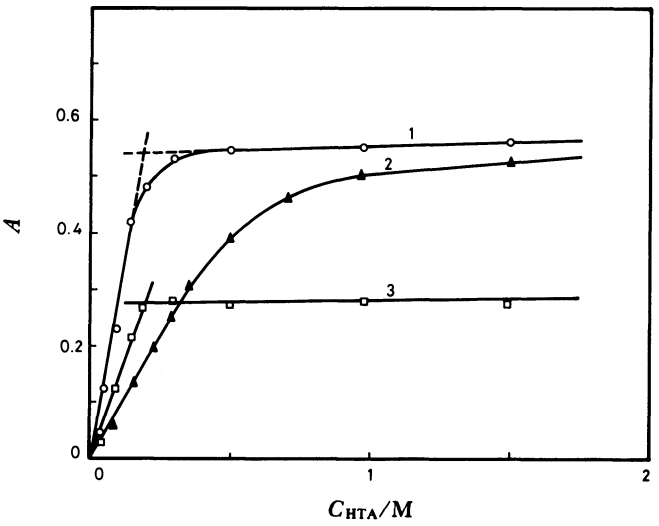

Fig. 1. Influence of total trichloroacetic acid concentration in the aqueous phase on benzene extraction of $PdHL^{3+}\cdot(TCA^-)_3$ ion-association compound. Concentrations in the aqueous phases: (1) and (2) 1.60×10^{-5} M Pd(II); 9.00×10^{-5} M 3,5-Cl2PADAB. (3) 4.60×10^{-5} M 3,5-Cl2PADAB. (1), (2), and (3) HTCA=variable; 1 M H_2SO_4; 10% ethanol. (1) λ_{max}= 600 nm, (2) λ_{max}=555 nm, (3) λ_{max}=440 nm. V_o= V_w=10 ml. Organic extracts diluted to 25 cm^3 with pure benzene after equilibrations. Time of full color development of $HLPd^{3+}$ complex=period of equilibration=45 min. Absorbance measures vs. (1) and (2) reagents, (3) water.

tion of both complex and reagent excess. With higher values the percentage extraction did not drop although strongly emulsified extracts were obtained. Ethanol was necessarily added in the aqueous phases together with the reagent. In 1 M HTCA with 1—2 M H_2SO_4 solutions, both the percentage extraction and color stability of the organic extracts do not change significantly up to 15% (v/v) ethanol concentration; whereas contents greather than the previous one disminish the extraction yield. Ethanol also stabilizes the extract color. The absorbance remains virtually unchanged for at least 10 h in its presence, but for only 20 min in its absence.

Still under the best experimental conditions, ethanol and HTCA were partially extracted by benzene, changing in this way the initial phase volumes. A strong scattering of absorbance measures was observed with phase volume changes. To increase reproducibility, a dilution step of the benzene extracts to a final fixed volume was included after extraction.

Periods of Color Development and Equilibration. In 1—2 M H_2SO_4 solutions with 1 M HTCA and 10% ethanol, Pd(II)-3,5-Cl2PADAB reaction was completed about 10 min after reagent addition. Being the complexation over, a few seconds' equilibration were required for the quantitative extraction. In practice, however, it was necessary to prolong both periods (color development and equilibration) to 15 min in

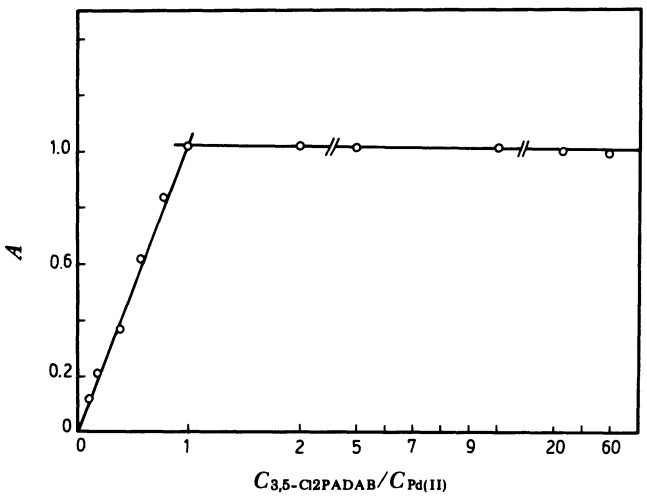

Fig. 2. Effect of 3,5-Cl2PADAB concentration on benzene extraction of $PdHL^{3+}\cdot(TCA^-)_3$ ion-association complex. Saturation curve. Concentrations in the aqueous phases: 3.00×10^{-5} M Pd(II); 3,5-Cl2PADAB=variable; HTCA 1 M; 1 M H_2SO_4; 10% ethanol. λ_{max}=600 nm. Reagent blank. Time of full color development=period of equilibration= 15 min. $V_o=V_w$=10 ml. Organic extracts diluted to 25 cm^3 with pure benzene after equilibrations.

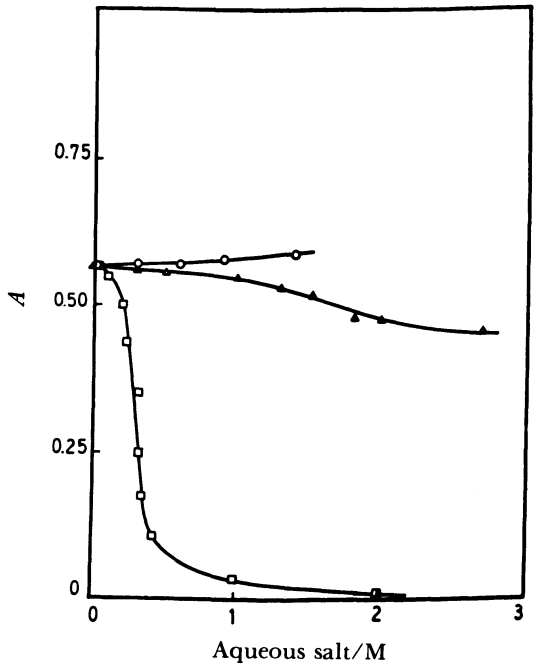

Fig. 3. Effect of aqueous salts on benzene extraction of the $PdHL^{3+}\cdot(TCA^-)_3$ association complex. Concentrations in the aqueous phases (10 cm^3): 1.60×10^{-5} M Pd(II); 1.60×10^{-4} M 3,5-Cl2PADAB; 1 M HTCA; 1 M H_2SO_4; 10% ethanol. (1) Na_2SO_4 (2) $NaClO_4$; (3) NaCl. λ_{max}=600 nm. Reagent blank. Organic extracts (10 cm^3) diluted to 25 cm^3 with pure benzene after equilibrations.

order not to obtain strongly emulsified benzene extracts.

Effect of Reagent Concentration. All other factors being kept constant, the reagent concentration was varied. It was found that a slight excess of reagent sufficed to extract completely the complex and to reach the maximum benzene extracts absorbance. Although this last magnitude remained unaltered for high 3,5-Cl2PADAB-to-Pd(II) ratios (Fig. 2), large amounts of reagent are not convenient because the absorption of reagent blanks becomes too high. Accordingly, 1 cm^3 of 0.025% (w/v) 3,5-Cl2PADAB solution every 10 cm^3 of aqueous phase is specified in the procedure. Figure 2 also shows that the extracted complex has high stability.

Influence of Foreign Salts. The influence of the salt content in the aqueous phases on the absorbance of the benzene extracts was studied by extracting Pd(II) in solutions where the H_2SO_4, 3,5-Cl2PADAB, HTCA, and ethanol concentrations were kept constant, and at the most convenient values. In separate test, different concentrations of sodium salts of sulfuric, perchloric, and hydrochloric acids were assayed. Figure 3 shows the results obtained. Chloride ions decrease the extraction yield and therefore, HCl cannot be recommended for dissolution of samples. Na_2SO_4 or $NaClO_4$ concentrations lower than 1 M influence significantly neither on the absorbance of benzene extracts of $PdHL^{3+}\cdot(TCA^-)_3$ nor on the yield of the extraction. For $NaClO_4$ concentrations higher than 1 M, the yield of the extraction diminishes due to the occlusion of Pd(II) and $PdHL^{3+}$ by the $NaClO_4$ crystals, precipited by the addition of the ethanolic solution of the reagent.

Beer's Law. Sensitivity. Under the experimental conditions described in the recommended procedure for the extraction-spectrophotometric determination of Pd(II), Beer's law is fulfilled up to a concentration of 2.16 ppm of Pd(II) in the organic extracts. The method's sensitivity, estimated according to Sandell's criterion, is 0.00123 μg of Pd(II) cm^{-2} for $\log(I_o/I_t)$= 0.001, and the apparent molar absorptivity of the ion-association compound extracted happened to be 8.6×10^4 $dm^3\,mol^{-1}\,cm^{-1}$ (s=900; $CL_{\alpha=0.05}^{85360-86640}$), at 600 nm. The reproducibility of the method, expressed by the percentual relative standard deviation, which was calculated on the basis of 20 determinations, is 0.59—0.39 depending on the metallic ion concentration.[5] The color of the diluted organic extracts is stable at least during 10 h.

Effect of Foreign Ions. The influence of foreign ions on the determination of Pd(II) by applying the proposed method, was studied for 18 cations that may generally appear with palladium in an analytical system, as well as for some common anions and masking agents. The criterion for interference was a change of ±3% in the absorbance for 2 ppm of palladium. Table 1 shows the results obtained. The greatest limitations are brought by Au(III). The interference of Au(III), when it is found in concen-

Table 1. Tolerances for Some Common Cations and Anions on Spectrophotometric Determination of Pd(II). Pd(II) taken=2 ppm

Ion	Ion-to-Pd(II) tolerated molar ratio[b]	Ion	Ion-to-Pd(II) tolerated molar ratio
Pt(IV)	1000	Mn(II)	3000
Ir(III)	10	Ag(I)	50
Ru(III)	2.5	Cd(II)	3000
Os(VIII)	5	Hg(II)	<1
Rh(III)	170	AsO_3^{3-}	6700
Au(III)	<1	Tartrate	4500
Cu(II)	300	Ascorbic acid	5000
Co(II)	500	SCN^-	1
Ni(II)	1000	Br^-	1
Fe(III)	1000	Co(II)[a]	5000
Fe(II)	2000	Ir(III)-(IV)[a]	400
Cr(III)	1000	Cu(II)[a]	5000
Zn(II)	1000	Ag(I)[a]	10000
Al(III)	3000		

a) Previous extraction with benzenic 0.02% (v/v) acetylacetone solution. b) Maximum tolerated values.

trations lower than 7 ppm, was avoided reducing it to metal by adding a few mg of solid $FeSO_4$, $NaNO_2$, Na_3AsO_3, or oxalic acid to its aqueous solutions and allowing the system to stand for 15 min before adding the reagent and HTCA. In higher concentrations, it was quantitatively extracted by means of Yoe and Overholser's technique[1,6] without change in the palladium concentration. Hg(II) interference could be controlled neither by masking nor by reducing it to metal; prior separation proved to be the only way of avoiding its interference. For that purpose, and in order to expand the method's applications to samples containing large amounts of Cr(III)-(VI), Os(IV)-(VIII), Ru(III)-(VIII), Cu(II), Co(II), Ir(III)-(IV), or Ag(I), several separative procedures were assayed. Volatilization[7,8] in hot concentrate H_2SO_4 or $HClO_4$ solutions proved to be the most efficient and practical method to separate mercury, chromium, osmium, and ruthenium. By combining the previous extraction of Pd(II) that uses acetylacetone dissolved in benzene[9] with the procedure suggested in this work, was the most convenient way for the Pd(II) determination in solutions containing high proportions of Cu(II), Co(II), Ir(III)-(IV), or Ag(I).

Volatilization Procedure. (i) Place 2—20 cm^3 of sample solution containing up to 50 μg of Pd(II) in an extraction tube. Add 10 cm^3 of 94—96% sulfuric acid and 10—15 drops of 72% $HClO_4$ and fume in hot plate until decoloration of the solution or reduction of the volume up to 5 cm^3. (ii) On reaching this stage, add carefully 20 cm^3 of a mixture solution of concentrate HCl and $HClO_4$ (1:8), drop by drop, and keep on heating. During the operation, stop adding the acid mixture whenever the sample color becomes greenish-grey, and keep on adding when it turns red-orange. (iii) Being the solution decolorized, go on heating until almost dried. Let it cool and then continue with the recommended procedure for Pd(II) determination.

If the sample had a great amount of chromium (up to 5.000 ppm) it was volatilized as chromyl chloride through the applications of steps (i) and (ii). But if only osmium and ruthenium occur (up to 6.000 ppm each), the steps to follow were just (i) and (iii). This procedure also enabled the removal of Hg(II) (as $HgCl_2$) up to 1.000 ppm by replacing in step (ii) the acid mixture by 30 cm^3 of 37% HCl.

Procedure Using Acetylacetone Dissolved in Benzene. Into an extraction tube place 20 cm^3 of solution containing between 10 and 100 μg of Pd(II). Adjust the pH to 0.5—0.8 with $HClO_4$ or NaOH solution. Next, add 20 cm^3 of benzenic 0.02% (v/v) acetylacetone solution and shake the tube for 30 min. Allow the phases to separate, and then shake 10 cm^3 of the benzene extract during 30 min with equal volume of an aqueous solution containing 1 M H_2SO_4, 1 M HTCA, 9×10^{-5} M 3,5-Cl2PADAB, and 10% ethanol. Afterwards, transfer the extract, by now colored, to a 25 cm^3 volumetric flask and dilute to the mark with pure benzene. Measure the absorbance of the benzene solution at 600 nm against a blank obtained in the same manner as described for the tests. Calculate the concentration of palladium from a calibration curve obtained under identical conditions.

Applications. The effectiveness of the one-step extraction procedure described in this paper, was evaluated by carrying out Pd(II) determinations on six synthetic solutions prepared from pure solutions of their components. Tables 2 and 3 outlines the compositions of the solutions and the results obtained. Sample No. 2 in Table 2 simulated, both in its compositions and in the component contents, the dissolution of a sample of a concentrate mineral of native platinum. A final stage of sample decomposition was simulated by repeated treatment (2—3 times) of the synthetic solution aliquots with portions of concentrate HCl-HNO_3 (3:1) mixture. Next, in order to eliminate completely osmium and virtual traces of chloride ions, these sample portions were heated until

Table 2. Results Obtained in the Benzene Extraction and Spectrophotometric Determination of Pd(II) with 3,5-Cl2PADAB and TCA^- in Synthetic Samples

Sample No.	Sample composition/% (w/w)	Solution/ppm	Pd(II) found[d]/ppm	E_r/%
1	Au (—)[a]	2000		
	Os (—)[b]	5000		
	Ru (—)[b]	2000		
	Pd (—)	1.50	1.49 ($s=1.4\times10^{-2}$ $Cl_{\alpha=0.05}^{1.51-1.49}$)	−0.66
2	Pt (87.47)	1081		
	Ir (1.24)	15.22		
	Os (0.48)[b]	6		
	Rh (0.25)	3		
	Au (0.02)[c]	0.5		
	Cu (0.71)	0.01		
	Fe (7.41)	91.6		
	Ni (0.10)	1.22		
	Pd (0.85)	9.95	9.86 ($s=1\times10^{-2}$ $Cl_{\alpha=0.05}^{9.88-9.85}$)	−1.00

a) Extracted into ethyl acetate in 3 M HCl solution. b) Volatilized as their respective tetroxides in hot 96% H_2SO_4 solution containing 10—15 drops of 72% $HClO_4$. c) Reduced to metal by adding solid FeSO. d) Mean of ten determinations ($n=10$) on five sample portions.

Table 3. Results Obtained in the Benzene Extraction and Spectrophotometric Determination of Pd(II) with 3,5-Cl2PADAB and TCA^- in Synthetic Samples. Previous Extraction of Pd(II) in pH 0.5—0.8 ($HClO_4$) Solutions with Acetylacetone Dissolved in Benzene

Sample No.	Sample composition/ppm		Pd(II) found[a]/ppm	E_r/%
1	Co(II)	2400		
	Pd(II)	0.80	0.79 ($s=6\times10^{-3}$ $Cl_{\alpha=0.05}^{0.794-0.785}$)	−1.80
2	Cu(II)	2500		
	Pd(II)	0.80	0.79 ($s=5\times10^{-3}$ $Cl_{\alpha=0.05}^{0.794-0.786}$)	−1.80
3	Ir(III)	580		
	Pd(II)	0.80	0.79 ($s=7\times10^{-3}$ $Cl_{\alpha=0.05}^{0.795-0.785}$)	−1.80
4	Ag(I)	17000		
	Pd(II)	1.61	1.62 ($s=3\times10^{-2}$ $Cl_{\alpha=0.05}^{1.63-1.58}$)	+0.62

a) Mean of ten determinations ($n=10$) on five sample portions.

dryness two times, upon adding 5 cm^3 of concentrate nitric acid containing 4—5 drops of 72% $HClO_4$. Before the color development stage, Au(III) and Ir(IV) were reduced to metal and Ir(III), respectively, by adding 20 mg of solid $FeSO_4$.

Sample No. 4 in Table 3 simulated, as far as its composition is concerned, the dissolution of a silver base alloy sample composed of 99.99% Ag and 0.01% Pd.

References

1) C. A. Fontán and C. B. Marone, *Anales Asoc. Quím. Argentina*, **71**, 449 (1983).

2) C. A. Fontán, C. B. Marone, and R. A. Olsina, Under consideration for publication.

3) G. Schwarzenbach and H. Flaschka, "Complexometric Titrations," ed by Methuen and Co., Ltd, London (1969).

4) American Chemical Specifications, "Reagents Chemicals," 4th ed., ACS (1964).

5) IUPAC, "Quantitative Characterization of Procedures Using Ultraviolet and Visible Molecular Absorption Spectrophotometry," *Pure Appl. Chem.*, **58**, 1015 (1986).

6) J. H. Yoe and L. G. Overholser, *J. Am. Chem. Soc.*, **61**, 2058 (1939).

7) F. E. Beamish, "The Analytical Chemistry of the Noble Metals," ed by Pergamon Press, 1st ed. (1966).

8) E. B. Sandell and H. Onishi, "Photometric Determination of Traces of Metals," Vol. III, part I, Jhon Wiley & Sons Inc., 4th. ed., U.S.A. (1978).

9) J. Stary, "The Solvent Extraction of Metal Chelates," ed by Pergamon Press, N.Y. (1964).