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### Authors

Clem, Ray G.  
Huffman, E.H.

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**University of California**  
**Ernest O. Lawrence**  
**Radiation Laboratory**

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DETERMINATION OF COPPER, NICKEL, AND PALLADIUM

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EXTRACTION OF METAL PYRIDINE AZIDES  
Spectrophotometric Determination of Copper, Nickel, and Palladium

Ray G. Clem and E. H. Huffman

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ABSTRACT

The isoelectronic nature of azide and thiocyanate ions, with the attendant similarities in forming metal complexes, suggests that pyridine-azide systems should have analytical applications similar to those of pyridine-thiocyanate systems. The efficiencies of extraction into chloroform of eleven metal pyridine azides are presented for the pH range from 2 to 11. Cobalt, nickel, copper, zinc, palladium, cadmium, platinum, and gold extract to the extent of 90% or more. Only 50% of the iron and 1% or less of the manganese and uranium are extracted. Copper, nickel, and palladium are determined by measuring the absorbances of the 10 ml. extracts in chloroform at 435 m $\mu$ , 320 m $\mu$ , and 325 m $\mu$ , respectively. The precisions for the determinations of 29 to 100  $\mu$ g. of copper, 56 to 197  $\mu$ g. of nickel, and 22 to 77  $\mu$ g. of palladium are 0.8%, 2.8%, and 1.1%, respectively. The details of color development and the interferences due to some common anions are given.

Complexes with pyridine and thiocyanate have been used for the extraction separation and determination of cobalt and nickel by Forsythe, Magee, and Wilson (6) and for the simultaneous determination of five transition elements by Ayres and Baird, who extracted the complexes into chloroform and measured the optical absorbances of the extracts (1). Approximate distribution ratios between the aqueous and organic phases were reported for three of the five metal complexes. The latter authors have given an extensive bibliography of the analytical uses of the pyridine thiocyanates which preceded their work, including some gravimetric methods. The azide and thiocyanate ions are isoelectronic and show many similarities in their abilities to form colored complexes with transition elements, and so one may expect similarities between pyridine-azide and pyridine-thiocyanate solutions in their chemical behavior. These expectations have been met in part, as shown herein. Metal pyridine azides have apparently not been reported previously, and it was thought to be of some interest to investigate possible analytical uses of such compounds.

The efficiencies of extraction into chloroform of pyridine azide complexes of eleven metals in the pH range from 2 to 11 are presented here; in addition, trace spectrophotometric methods for determining three of these metals in the chloroform phase are reported. Copper, nickel, and palladium are determined at their maximum absorbances of 435 m $\mu$ , 320 m $\mu$ , and 325 m $\mu$ , respectively, with optimum ranges of 29 to 100  $\mu$ g., 56 to 197  $\mu$ g., and 22 to 77  $\mu$ g., respectively, per 10 ml. of chloroform extract.

The metal pyridine azides which are readily extracted into chloroform are also insoluble in water, but the explosive nature of these compounds precluded the study of gravimetric methods for analytical use.

Table I. Methods of Analysis

<u>Metal</u>	<u>Method</u> <sup>*</sup>	<u>Reference</u>
Mn	$\text{IO}_4^-$ (S)	(14)
Fe	1,10 phenanthroline (S)	(13)
Co	$\text{SCN}^-$ (S)	(12)
Ni	Pyridine-azide (S)	This paper
Cu	Pyridine-azide (S)	This paper
Zn	$\text{NH}_3\text{-NH}_4\text{Cl}$ (P)	(7)
Pd	$\text{N}_3^-$ (S)	(2)
Cd	$\text{NH}_3\text{-NH}_4\text{Cl}$ (P)	(7)
Pt	$\text{SnCl}_2$ (S)	(15)
Au	$\text{N}_3^-$ (S)	(4)
U	$\text{SCN}^-$ (S)	(5)
$\text{N}_3^-$	$\text{Fe}^{3+}$ (S)	(10)

\* (S) = spectrophotometric

(P) = polarographic

### EXPERIMENTAL

Apparatus. All absorbance measurements and spectral scans were made with a Beckman DU spectrophotometer equipped with a photomultiplier tube and a deuterium lamp, using 1.00 cm. silica cells. The pH measurements were made with a Beckman Model 76 expanded scale pH meter, using an E2 electrode. All polarographic analyses were made with a Leeds and Northrup Type E Electro-Chemograph. Separatory funnels with Teflon stopcocks were used to avoid grease contamination of the chloroform phase.

Reagents and Analyses. All materials used were of reagent quality unless otherwise specified. Solutions of palladium and gold in hydrochloric acid were prepared from the metals described previously (2,4). Platinum and manganese were also used as their chlorides. Uranyl nitrate was prepared from  $U_3O_8$  (N.B.S. assay 99.95%). Copper and nickel perchlorate solutions were prepared by dissolving weighed amounts of metal in nitric acid and fuming with a small excess of perchloric acid. All other metals were converted to their perchlorate salts.

Sodium azide (Fisher's Purified), 99.2% purity as determined by the hydrogen ion consumed on oxidation with nitrite (3), was used to make 1.00 M solutions. Matheson's lecture bottle nitrogen was used for the polarographic analyses.

A resume of methods of analysis employed in obtaining the extraction efficiencies is given in Table I. In addition, the larger amount of nickel from the extraction at pH 5 was determined gravimetrically with dimethylglyoxime.



Preliminary Tests. Iron, cobalt, nickel, copper, palladium, platinum, gold, and uranium were observed to be extracted from nearly neutral solutions containing both pyridine and azide, as evidenced by the transfer of color from the aqueous to the chloroform phase. The presence of pyridine alone or azide alone did not cause the color transfer. Zinc and cadmium were found to be but slightly extracted when only pyridine or azide was present, but the extractions were greatly enhanced by the presence of both pyridine and azide. Neither chromium(III) nor vanadium(V) were extracted, based on visual observations, when both pyridine and azide were present. On standing, the gold extract underwent reduction to the metal and the color intensity of the yellow cobalt extract increased, but there were no visible changes in the extracts of the other metals.

Recommended Procedures for Copper, Nickel, and Palladium. Add the weakly acidic solution (pH 1-2) containing 29-100  $\mu\text{g.}$  of copper, 56-197  $\mu\text{g.}$  of nickel, or 22-77  $\mu\text{g.}$  of palladium to a 125-ml. separatory funnel; add 1 ml. of pyridine and 2 ml. of 1.00 M sodium azide, and adjust the volume to 10 ml.. Adjust the pH in the range from 5 to 7 for copper or from 8.5 to 11 for nickel. If the palladium sample contains no other buffering agent, add 12 drops (about 0.3 ml.) of concentrated sulfuric acid, which will give a pH of  $4.67 \pm 0.10$ . If a foreign buffer ion is present, adjust the pH using a narrow range pH paper. Add 10 ml. of chloroform and shake for 30 seconds.

Drain a sufficient amount of the chloroform extract to fill a 1.00 cm. absorbance cell through a small cotton tuft supported on a micro-funnel. Measure the absorbance of the extract at 435  $\text{m}\mu$ . for copper, 320  $\text{m}\mu$ . for nickel, or 325  $\text{m}\mu$ . for palladium against a blank extract prepared in the same manner. Prepare a calibration curve by carrying known amounts of metal ion through the same procedure.

## RESULTS

Extraction. The concentrations of pyridine and azide, 1.12 M and 0.200 M, respectively, used throughout the extraction studies were those sufficient to give optimum color development with copper, nickel, and palladium. In all instances the volume ratio of chloroform to aqueous phase was 1:1, before equilibration, and the pH was adjusted with either sodium hydroxide or sulfuric acid. The pH values given in Table II were obtained prior to equilibration, and no attempt was made to maintain constant ionic strength. The onset of hydrolysis was generally signaled by a decrease in the amount of metal extracted at pH values greater than optimum; however, extraction was continued to a pH value at which solid material appeared after equilibration. In some cases the decrease was gradual, as with palladium; in other cases it was abrupt, as with copper.

Consistent results were obtained in all cases, except for platinum, using a 30 second equilibration time. Shortly after the addition of the reagents to a chloroplatinate solution, a turbidity appeared. After shaking and phase separation, a clear solution was first obtained, but the turbidity gradually reappeared in the aqueous layer. It was necessary to shake the chloroplatinate solution with the chloroform a total of nine times, 30 seconds each, over a period of one half hour in order to reach equilibrium. This behavior probably allows a cleaner separation of palladium and gold from platinum than would be expected from the equilibrium extraction values shown in Table II. Data for the last column were obtained by equilibration of 10 ml. each of the organic and aqueous phases containing no extractable metal ions. The gold extracts must be sampled soon after equilibration, since gold is reduced on standing.

Table II.

pH	% Extraction												V <sub>aq</sub> :V <sub>org</sub>
	Mn <sup>*</sup>	Fe <sup>3+</sup>	Co <sup>*</sup>	Ni <sup>2+</sup>	Cu <sup>2+</sup>	Zn <sup>2+</sup>	Pd <sup>2+</sup>	Cd <sup>2+</sup>	Pt <sup>2+</sup>	Au <sup>3+</sup>	UO <sub>2</sub> <sup>2+</sup>	N <sub>3</sub> <sup>-</sup>	
2	0.0	0.0	0.2	<0.1	<0.1	0.0	98.8	0.0	79.9	92.0	<0.1	47	9.5:10.5
3	0.0	0.0	0.4	0.1	1.8	0.0	98.9	0.0	92.4	98.2	<0.1	41	9.5:10.5
4	0.0	0.6	0.8	0.3	72.8	0.0	98.9	0.8	95.5	98.4	<0.1	37	9.4:10.6
5	0.0	50.0	2.5	51.6	98.1	2.9	99.4	7.4	94.6	98.9	<0.1	25	9.2:10.8
6	<0.1	ppt.	84.0	98.7	99.4	73.2	99.7	85.0	85.9	98.9	1.1	19	8.8:11.2
7	0.1	-	95.0	99.9	99.5	93.3	99.8	91.4	75.6	98.9	ppt.	2	8.7:11.3
8	0.2	-	95.7	>99.9	99.6	93.7	99.8	91.6	72.3	98.6	-	0.3	8.6:11.4
9	0.2	-	95.4	>99.9	99.8	ppt.	99.8	90.2	70.9	98.3	-	0.0	8.6:11.4
10	ppt.	-	ppt.	99.6	98.2	-	98.9	89.1	70.1	98.0	-	0.0	8.6:11.4
11	-	-	-	99.5	ppt.	-	97.6	ppt.	68.7	97.6	-	0.0	8.6:11.4
mg./10 ml.	10.64	2.00	5.00	4.67	2.03	10.00	4.00	4.00	2.79	5.00	10.00 as U	84.0	

\* Oxidation state may be 2+ or higher, depending on pH and air oxidation.

After equilibration the metal-poor phase was taken for analysis. Except for copper, cadmium, nickel and zinc, pyridine was removed prior to analysis by making the solution basic and evaporating under a heat lamp. Azide was removed as hydrazoic acid by acidifying and heating the solution. Palladium complexes pyridine strongly, so it was necessary to make a second basic evaporation in the presence of sodium hypochlorite to effect complete removal of pyridine (16). Cobalt(II) also complexes pyridine strongly and probably undergoes air oxidation to the trivalent state. This behavior causes difficulties in the analysis of cobalt by the thiocyanate method. However, if the complex is heated to fumes with sulfuric and nitric acids, the azide is removed, cobalt returns to the divalent state, and pyridine is converted to pyridinium sulfate. No troubles are then encountered in the cobalt analysis, provided the pH is not increased above the pyridinium ion equivalence point.

Color Development. Moderately small amounts of copper, nickel, and palladium may be determined after chloroform extraction by the recommended procedures; so the details of color development were studied for only these three elements. The amount of each metal used in studying the variables was sufficient to give an absorbance about mid-way in the optimum range, under the conditions described for the recommended procedures. Spectral scans for chloroform extracts of copper, nickel, and palladium are shown in Figure 1.

To study the effect of pH on absorbance, the pyridine and azide concentrations were held at 1.12 M and 0.200 M, respectively; these concentrations were found to be sufficient to give optimum color development for all three metals. The pH was adjusted with concentrated sulfuric acid or 10 M sodium hydroxide; perchloric acid could not be used because of the low solubility of pyridinium perchlorate. After equilibration of the solutions for 30 seconds

with an equal volume of chloroform, the absorbances of the organic phases were obtained. The results are shown in Figures 2, 3, and 4. It seems likely that a number of different complexes exist in the chloroform phase, since the variation in absorbance cannot be explained in terms of volume change, blank variation, or amount of metal extracting. As shown in Figures 3 and 4, the blank increases at lower pH values due to extraction of hydrazoic acid, as per Table I. The blank absorbance at high pH values is due to the extraction of pyridine(1). The blank values vary from batch to batch of both pyridine and chloroform, so the unknown and the calibration curve should be read using the same reagent stocks.

The absorbance of copper may be read at pH values from 5 to 7, on a plateau where there is little variation (Figure 2). The plateau region from pH 8.5 to pH 11 was selected for the determination of nickel because of the difficulty of making an adjustment to exactly pH 5.5 for the maximum absorbance (Figure 3). The curve for palladium shows no pronounced plateau, after subtracting the blank. However, there is a range from pH 4 to pH 6 in which the absorbance variation is about 6%, after subtracting the blank. Both hydrazoic acid and the pyridinium ion have their  $pK_a$  values near the middle of this range and, under the conditions for the procedure given above, a pH of  $4.67 \pm 0.10$  was attained by the addition of a constant amount of strong acid to both sample and blank. Thus it was possible to make use of this pH interval for the determination of palladium with satisfactory precision.

The azide and pyridine requirements for optimum absorbances were examined with the pH levels held within optimum limits. For either copper or nickel there is a plateau in absorbance for azide concentrations between 0.1 M

and 0.3 M. The copper absorbance is increased by 2% and the nickel absorbance by 5% at the 0.5 M azide level; losses of 53% and 12%, respectively, occur with 0.01 M azide. A maximum absorbance, with no level region, is found for palladium at 0.2 M azide. The absorbance decreases from the optimum value at both higher and lower azide concentrations; e.g., the loss is 4% in 0.5 M azide and 76% in 0.01 M azide.

Copper and nickel exhibit gains in absorbance of 12% and 72%, respectively, when the pyridine concentration is increased from 0.1 M to 0.6 M, after which the absorbance remains constant to 1.1 M. At the 2.2 M pyridine level, a loss of 4% in absorbance was noted. With palladium, an absorbance plateau was found from 1.1 M to 2.2 M pyridine. A maximum, 4% higher than the plateau, occurs with 0.1 M pyridine and the color intensity decreases by 6% from the plateau at 3.3 M. Considering the efficiency with which pyridine is extracted into chloroform, an excess over that necessary for optimum color development only serves to decrease the color intensity by dilution.

Precision and Interferences. Table III gives the reproducibility obtained using the recommended methods. The absorptivity coefficients are  $0.0697 \pm 0.0005$  p.p.m.<sup>-1</sup> cm.<sup>-1</sup> for copper,  $0.0355 \pm 0.0010$  for nickel, and  $0.0913 \pm 0.0010$  for palladium, based on the initial 10 ml. of organic phase. The absorptivity coefficient varies with the pH if based on the volume after equilibration (Table I). The anticipated errors for concentrations covering the optimum absorption range are 0.8%, 2.8%, and 1.1%, based upon the standard deviations of the absorptivity coefficients for copper, nickel, and palladium, respectively.

In Table IV are listed the maximum concentrations of anions which will give less than a 3% error in the determinations of the three metals.

Table III. Reproducibility

<u>µg. copper</u>		<u>µg. nickel</u>		<u>µg. palladium</u>	
Added	Found	Added	Found	Added	Found
20.3	20.1	62.3	63.4	20.0	19.9
20.3	20.4	62.3	59.2	20.0	20.3
40.6	40.2	93.4	95.8	30.0	30.1
40.6	40.9	93.4	97.2	30.0	30.1
60.9	60.3	124.5	127.3	40.0	40.5
60.9	60.7	124.5	126.2	40.0	40.5
81.2	81.5	155.7	156.9	50.0	50.6
81.2	80.6	155.7	152.1	50.0	50.2
101.5	101.5	186.8	191.5	60.0	60.1
101.5	101.5	186.8	188.7	60.0	59.5
121.8	121.9	217.9	219.7	70.0	68.8
121.8	123.4	217.9	225.4	70.0	69.0
				80.0	79.0
				80.0	79.1

Table IV. Tolerance for Anions

	Max. molarity giving less than 3% error				
	$\text{Cl}^-$	$\text{ClO}_4^-$	$\text{PO}_4^{3-}$	$\text{SO}_4^{2-}$	$\text{C}_4\text{H}_4\text{O}_6^{2-}$
Cu	1.3	0.5	0.6	0.9	0.1
Ni	2.8	0.4	0.5	0.7	0.7
Pd	1.2	0.2	1.2	1.1	0.5



A loss of 5% in the intensity of the copper color occurs at a tartrate concentration of 0.4 M, but the absorbance remains constant from 0.4 M to 0.6 M. This allows the use of up to 0.6 M tartrate when needed to mask other cations, such as iron, if the same concentration of tartrate is used in preparing the calibration curve.

The volume ratio of aqueous phase to organic phase may be increased to 2:1 for copper, 3:1 for nickel, and 2:1 for palladium and still give an error of less than 3%. These volume ratio effects were determined by keeping the amounts of metal ions and the concentrations of reagents constant, and using corresponding blanks.

#### DISCUSSION

The data presented indicate some separations of general analytical interest and, in comparison to the pyridine-thiocyanate reagent, the pyridine-azide reagent has two advantages. There is no change in the absorbance of the blank up to 17 hours, and the excess azide is easy to remove by acidification and warming or by oxidation to nitrogen gas. The selectivity might be improved by the use of other solvents or other amines, as well as by variation in both azide and pyridine concentrations. The use of masking agents can undoubtedly be used to improve selectivity. For example, when the aqueous phase is 0.1 M in tartrate, the extraction of iron(III) is essentially prevented; only 0.4% of the iron(III) extracts at pH 6 and less than 0.1% at all other pH values from 2 to 11.

Both cobalt and gold were investigated briefly for possible trace method development. The gold extract is not sufficiently stable to warrant

further investigation; the color fades rapidly and reduced gold later appears at the phase interface. Cobalt(II) apparently undergoes oxidation in the chloroform phase. When microgram amounts are first extracted the absorbance maximum is at 355  $\mu$ ., but on standing the maximum shifts to 370  $\mu$ . and the absorbance increases. The color intensity is not reproducible enough to allow the development of a method. If the extract is shaken with 3% hydrogen peroxide the color intensity again increases in an erratic manner, but if the aqueous phase is made 3% in hydrogen peroxide and warmed, very little extraction occurs.

The compositions of the complexes encountered here are not known, although some indications are given. Pyridine and thiocyanate react with some divalent metal ions to form water insoluble complexes of the composition  $M(C_5H_5N)_2$  or  $4(SCN)_2$  (1,6), and it is probable that analogous compounds are formed with azide in many cases. All of the metals having appreciable extraction characteristics react with the pyridine-azide reagent to form compounds which are only slightly soluble in water.

Attempts to elucidate the nature of the copper species extractable in chloroform were not conclusive. A spectral scan of an aqueous solution containing  $1 \times 10^{-4}$  M  $Cu^{++}$  and 0.2 M  $N_3^-$  has the same shape, with maximum absorbance at 385  $\mu$ ., as has the scan for a solution which is also 1.1 M in pyridine. It thus appears that no pyridine-containing complex is present in the aqueous phase, though pyridine is necessary for the extraction of copper. A mole ratio plot using  $1 \times 10^{-3}$  M  $Cu^{++}$ , with the absorbance peak at 370  $\mu$ , shows a 1:4 copper to azide species in the presence of  $4.46 \times 10^{-2}$  M pyridine. Saini and Ostacoli (11) found the same ratio in a mixture of 2-ethoxyethanol and water, but containing no pyridine. The green chloroform extract leaves a brown residue

upon evaporation with dry nitrogen. The green color gradually returns when the brown residue is stored over pyridine for three days. Ratios of copper to azide found on analysis (3) were 1:1.80 and 1:1.61, but the milligram amounts of sample which could be worked with safely were insufficient to obtain reliable results on a pyridine analysis. Vapor pressure measurements, as used for copper pyridine nitrates (9), would probably give an indication of the varying pyridine content of the solid.

LITERATURE CITED

- (1) Ayres, G. H., Baird, S. S., *Talanta* 7, 237 (1961).
- (2) Clem, R. G., Huffman, E. H., *Anal. Chem.* 37, 86 (1965).
- (3) *Ibid.*, p. 366.
- (4) *Ibid.*, p. 1155.
- (5) Currah, J. E., Beamish, F. E., *Ibid.*, 19, 609 (1947).
- (6) Forsythe, J. H. W., Magee, R. J., Wilson, C. L., *Talanta* 1, 249 (1958).
- (7) Kolthoff, I. M., Lingane, J. J., "Polarography", Vol. 2, p. 504, Interscience, New York (1952).
- (8) Mellan, I., "Organic Reagents in Inorganic Analysis", p. 179, Blakiston, Philadelphia (1941).
- (9) Mitra, N. G., Sinha, P. C., *J. Indian Chem. Soc.* 27, 29 (1950).
- (10) Roberson, C. E., Austin, C. M., *Anal. Chem.* 29, 854 (1957).
- (11) Saini, G., Ostacoli, G., *J. Inorg. Nucl. Chem.* 8, 346 (1958).
- (12) Sandell, E. B., "Colorimetric Determination of Traces of Metals", 3rd ed., p. 426 (1959).
- (13) *Ibid.*, p. 546.
- (14) *Ibid.*, p. 610.
- (15) *Ibid.*, p. 728.
- (16) Whitmore, F. C., "Organic Chemistry", 2nd ed., Vol. 2, p. 783, Dover, New York (1951).

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FIGURE CAPTIONS

Fig. 1. Absorption spectra of chloroform extracts

Aqueous phase: 0.2 M azide; 1.1 M pyridine;

70  $\mu\text{g. Cu}^{++}$ , 90  $\mu\text{g. Ni}^{++}$ , or 82  $\mu\text{g. Pd}^{++}$  per 10 ml.

Readings vs. extracts of blanks containing all reagents

Fig. 2. Effect of pH on color development for copper at 435  $\text{m}\mu$

Fig. 3. Effect of pH on color development for nickel at 320  $\text{m}\mu$

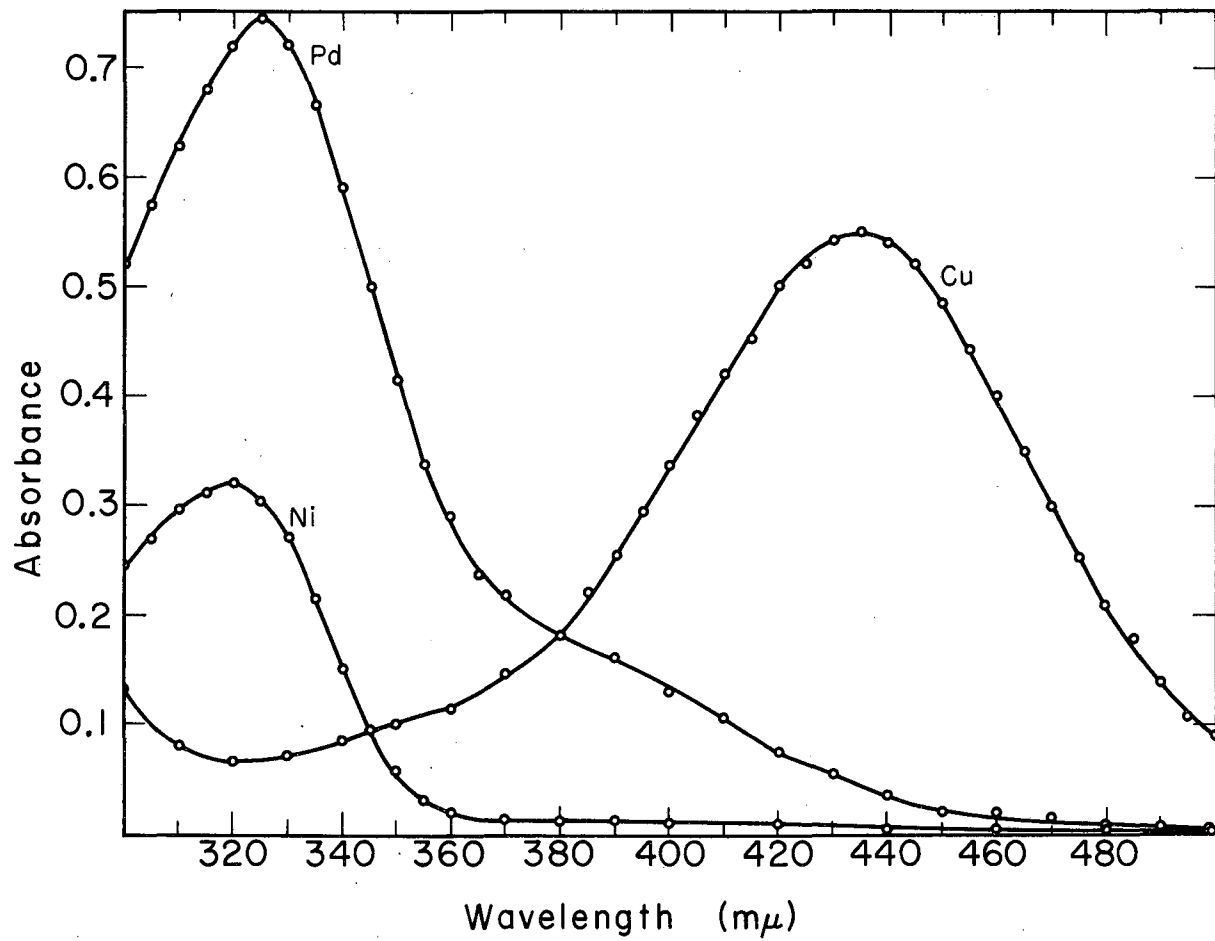
(A) nickel extract vs. blank extract

(B) blank extract vs. chloroform

Fig. 4. Effect of pH on color development for palladium at 325  $\text{m}\mu$

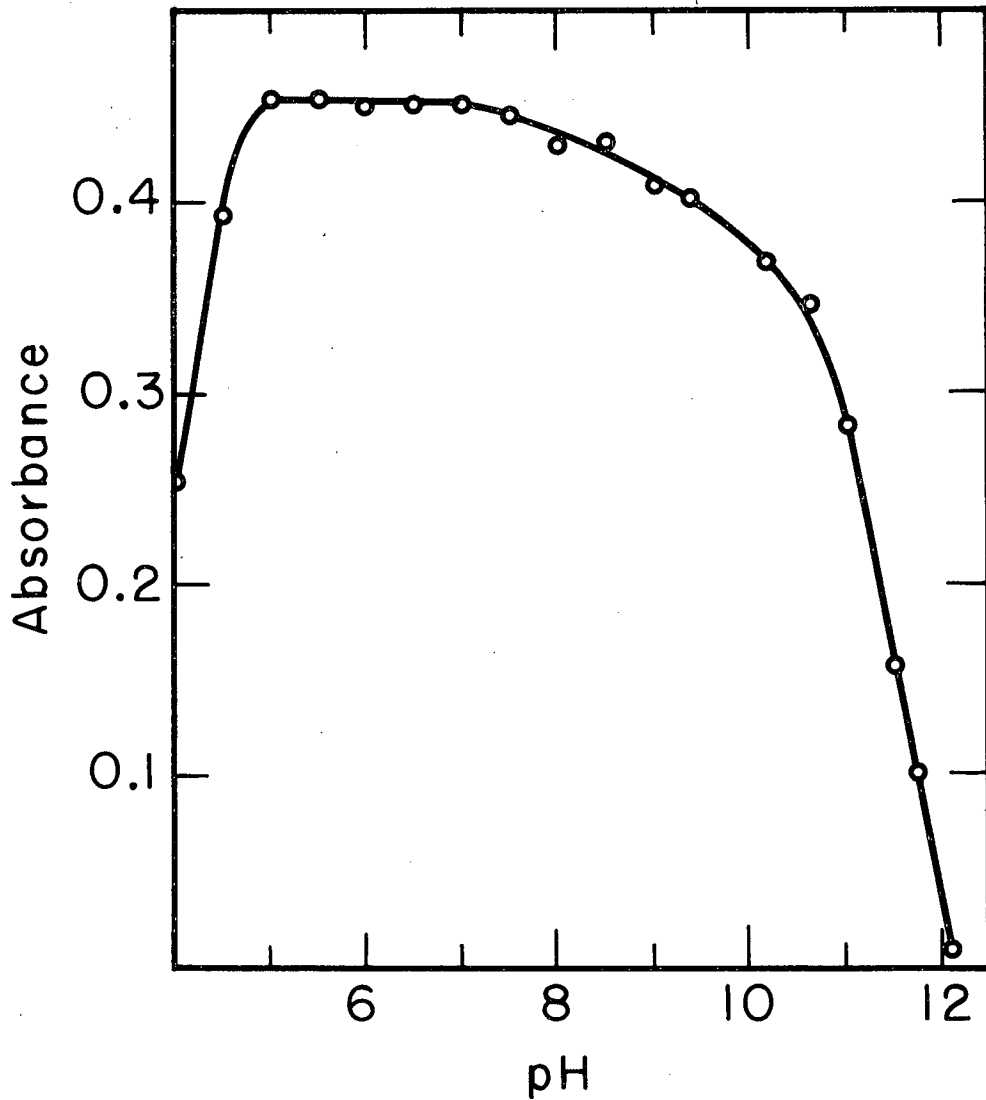
(A) palladium extract vs. blank extract

(B) blank extract vs. chloroform



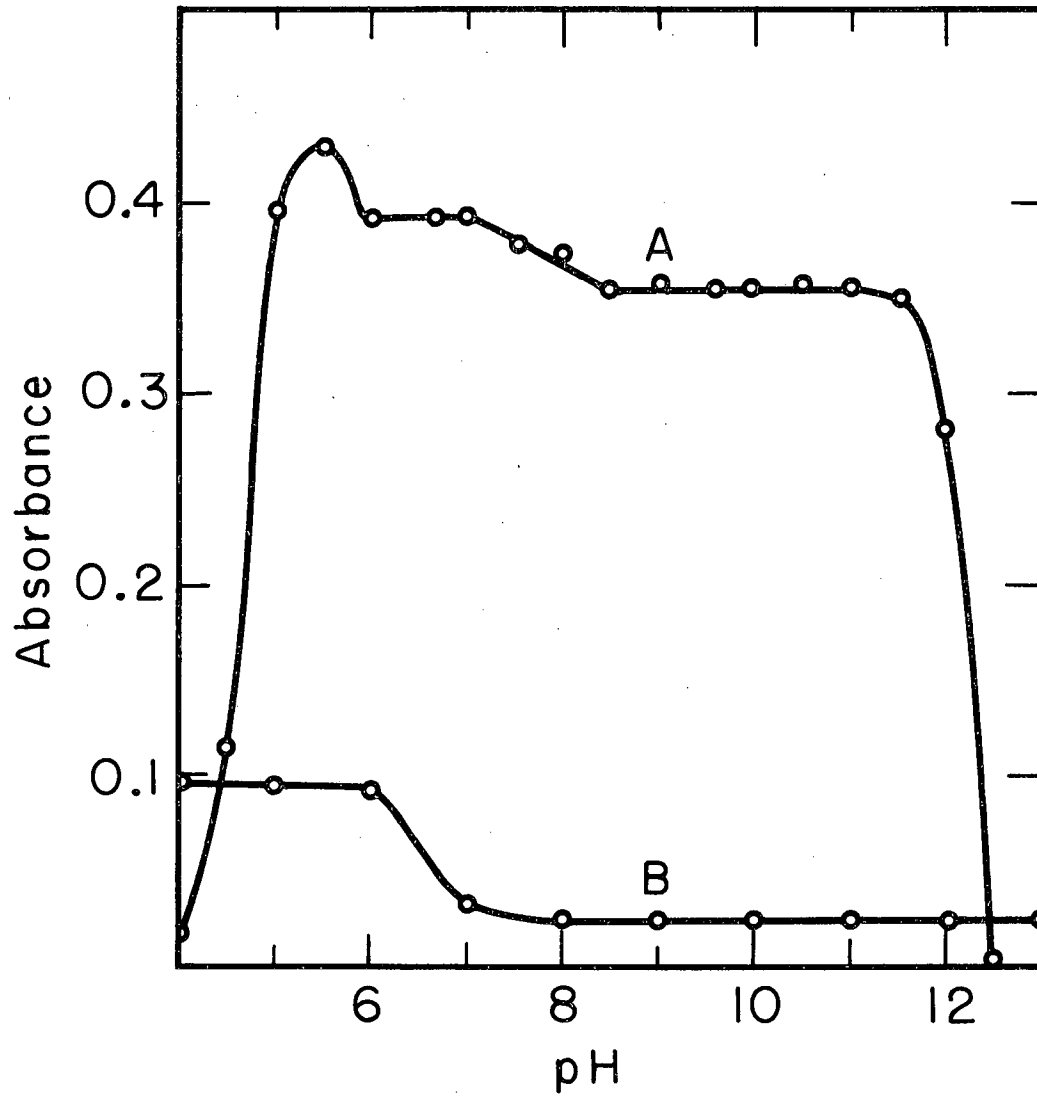
MUB-9311

Fig. 1



MUB-9312

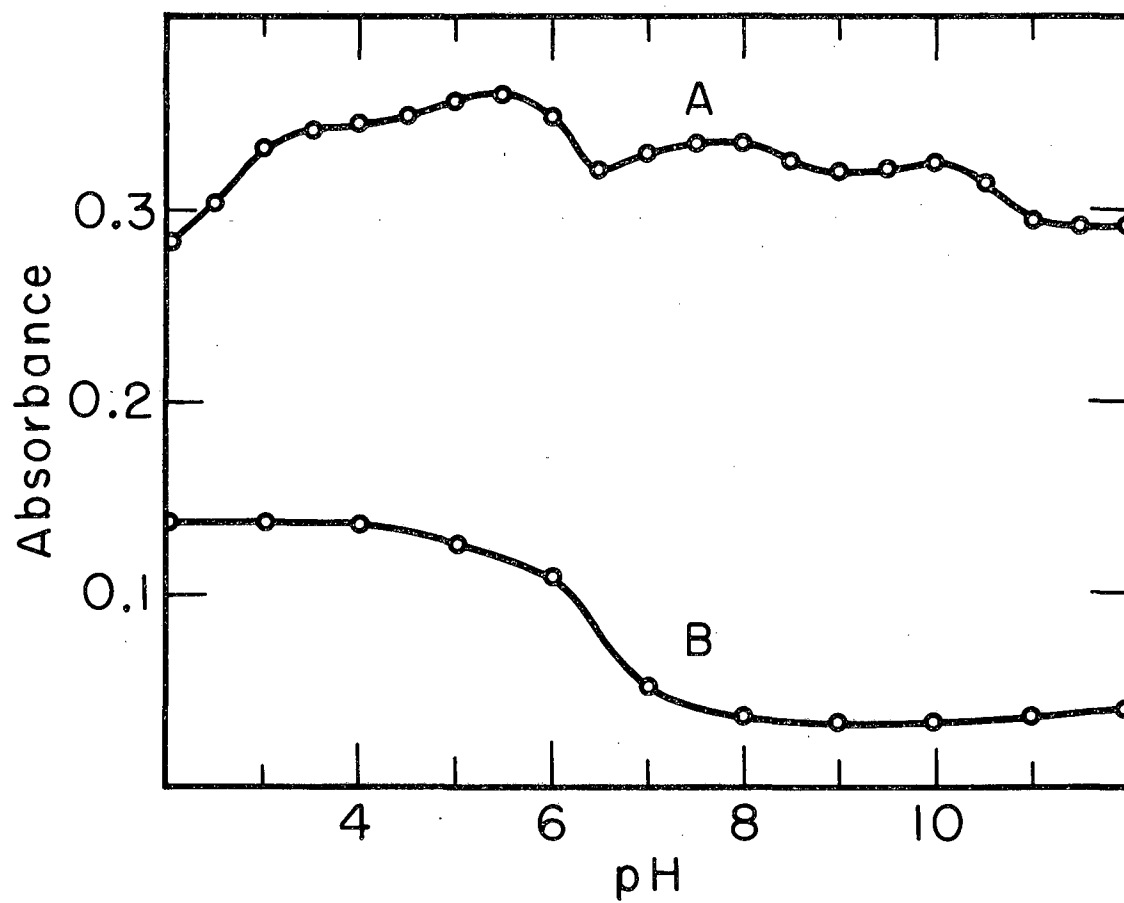
Fig. 2



MUB-9313

Fig. 3





MUB-9314

Fig. 4

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