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ABSTRACT

A spectrophotometric method for the determination of palladium is presented which utilizes the absorptivity of the tetraazidopalladium (II) complex at 315 mμ. after extraction into n-butyl alcohol and back-extraction into water. The main factors which control the color development and extraction are discussed and the effects of some common foreign ions are shown. The method offers advantages in sensitivity, color stability, speed and accuracy. The standard deviation over the optimum range from 1.3 to 4.6 p.p.m. is 0.03 p.p.m.

A number of colorimetric methods are known for the determination of
small amounts of palladium (1,7). In general these methods have one or more
of the following drawbacks: slow development of color, fading of the color
within a short time so that standards must be made frequently, low sensitivity,
oxidation of the color forming reagent by air, narrow pH range for extraction
and color development and low tolerance for other cations. The purpose of
this paper is to present a simple, rapid and accurate extraction-stripping
method for the spectrophotometric determination of palladium by azide ion,
with an optimum range of 1.3 to 4.6 p.p.m. for a 1.00 cm. cell. The color is
formed immediately and the calibration standards are stable for months. In
contrast to commonly accepted methods of comparable sensitivity, this method
can tolerate the presence of centigram quantities of several of the more com-
mon base metals and milligram to decimilligram amounts of gold and the plati-
num metals, except platinum itself. Silver, lead and platinum interfere and
must be removed prior to analysis.

Spectrophotometric studies by Sherif and Michail (8) of the azide-
palladium system in the visible spectral region revealed that the diazido,
tetraazido and, possibly, the monoazido palladium (II) species exist in water
or in water-acetone mixtures. The molar absorptivity reported does not appear
to merrit development of an analytical method using the visible spectrum.
Investigations in this laboratory in the near ultraviolet spectral region have
been reported to show the probable existence of the penta- and hexaazido
palladium (II) species in ethanol (2). The tetraazido species, used as the
basis for the analytical method presented here, exhibited an absorbance peak
at 315 mμ with a high molar absorptivity in aqueous solutions. It can be
extracted into n-butyl alcohol from acidic azide solutions and back-extracted
into neutral azide solutions.

EXPERIMENTAL

Apparatus. All absorbance measurements and spectrum scans were made with a Beckman DU spectrophotometer equipped with a photomultiplier tube, using matched 1.00 cm. silica cells. The pH measurements were made with a Beckman Model 76 Expanded Scale pH meter. Separatory funnels with Teflon stopcocks were used to avoid contamination of the organic solvents with grease.

Reagents. Reagent grade chemicals were used unless otherwise specified. A 0.1000 gram quantity of shiny, spectroscopically pure palladium metal sheet was dissolved in hot aqua regia and boiled repeatedly with concentrated hydrochloric acid until all nitrate was expelled, as shown by the brucine test (3). After evaporation to near dryness the residue was taken up in a minimum amount of hydrochloric acid and made to 100 ml.. A working solution containing 25 µg. palladium per ml. was obtained by dilution of the stock solution.

Practical grade sodium azide, with a 98.5% purity as determined by the Volhard method, was recrystallized by the Pepkowitz procedure (6) and a 0.50 $\underline{M}$ solution prepared.

A buffer of pH 6.5 was prepared from disodium phosphate heptahydrate and monosodium phosphate monohydrate, 0.5 $\underline{M}$ in each. The pH may vary from 6.3 to 6.6 depending upon the exact water content of the salts used, but this variation is of no consequence.

The common cations used in the interference studies were in the form of either chloride or sulfate salts. The anions were in the form of either sodium or potassium salts. Platinum metals, with a purity of 99.8% or higher, were made soluble by a chlorination procedure (4).

Preliminary Tests. At the outset it was observed that the yellow palladium azide complex, which forms immediately, could be extracted into n-butyl alcohol and isoamyl alcohol from acidic azide solutions, but only in

the case of n-butyl alcohol could the color be back extracted into neutral aqueous azide solutions. The isoamyl alcohol resisted stripping of palladium even at pH 11-12. Among other solvents tried as extractants without success were ethyl and diisopropyl ethers and diisobutyl and methyl ethyl ketones. The solubility of n-butyl alcohol in water is 10% and it forms an emulsion, when shaken with water alone, which separates very slowly. The addition of a high concentration of an indifferent salt suppresses the water solubility and effects a rapid phase separation.

Recommended Procedure. Evaporate samples containing 40-115 mg. palladium, from which excessive amounts of interfering elements have been removed, to near dryness twice under a heat lamp with 2-3 drops of concentrated sulfuric acid or 6-8 drops of 85% phosphoric acid, and cool. The selection of acid depends upon the cation solubilities involved. Transfer the solution to a 125 ml. separatory funnel; add 2 ml. of 0.50 $\underline{M}$ sodium azide and 5 ml. of either 1.0 $\underline{M}$ sodium bisulfate or 1.0 $\underline{M}$ monosodium phosphate. Adjust the volume to 10-15 ml. and test the pH, which should be below 2.7, with pHydrion paper. Add 10 ml. of n-butyl alcohol and extract the palladium by shaking vigorously for one minute. Discard the aqueous layer. Rinse the extract with 10-15 ml. of an aqueous solution containing azide, salt and acid as above.

Add 1 ml. of 0.50 $\underline{M}$ sodium azide to the organic phase, swirl briefly and then add 10 ml. of pH 6.5 buffer. Back-extract the palladium by shaking vigorously for one minute and drain the aqueous phase into a 25 ml. volumetric flask. Rinse the funnel once by shaking for 5 seconds with 3-5 ml. of water and once with one ml. of 0.50 $\underline{M}$ sodium azide plus 5 ml. of the buffer solution. Add these rinsings to the flask and make to volume.

To each of five 125 ml. separatory funnels add one to five ml. of the solution containing 25 µg. palladium per ml., then continue as described above for the extraction and stripping. Against a blank containing all

components but palladium (the blank need not be extracted), obtain and plot

the absorbances of the five solutions versus the concentrations. The same

calibration curve is obtained regardless of whether sulfuric or phosphoric

acid is used in the preparation of the solution for extraction. If it is

known that no interfering ions are present, the color may be developed without

extraction of either the sample or the standards for calibration.

RESULTS

Spectrum scans are shown in Figure 1 for the palladium azide complex

in water and in n-butyl alcohol extracts, as well as for the reagents used in

the color development. The concentrations of azide and of phosphate scanned

are 25 and 1.7 times, respectively, the concentrations present after color

development. Beer's Law is obeyed by the aqueous solution over the concentra-

tion range from 1 to 5 p.p.m. The optimum range for 1.00 cm. cells is from

1.3 to 4.6 µg. palladium per ml..

Several solutions prepared over the range of 1-5 p.p.m. gave an ab-

sorptivity of 0.155 p.p.m.$^{-1}$ cm.$^{-1}$ with a standard deviation of 0.002, cor-

responding to a 1.3% relative standard error. A study of deviation on 17

samples varying from 2 to 4 p.p.m. gave the results shown in Table I.

Table I. Reproducibility

Pd added, p.p.m.	2.00	3.00	4.00
Pd found, p.p.m., ave.	2.03	3.00	3.94
Range	2.01-2.04	2.95-3.07	3.77-4.04
No. samples	5	5	7
Standard deviation, p.p.m.	0.046	0.044	0.029
Relative std. dev.	2.3	1.5	0.7
Std. dev. pooled, p.p.m.	0.032		

COLOR DEVELOPMENT

The following tests were made with 100 μg. (4 p.p.m.) palladium except in the last series, as noted, and the effects were obtained by developing the color without extraction.

Effect of Azide Concentration. When the azide concentration was varied from 0.001 $\underline{M}$ to 0.1 $\underline{M}$ in small increments, the color intensity increased rapidly up to 0.008 $\underline{M}$ azide, after which it became constant. Three solutions, with azide concentrations of 0.001 $\underline{M}$, 0.01 $\underline{M}$ and 0.1 $\underline{M}$, were allowed to stand for two months. The absorbance values of the last two solutions did not change during this time but the 0.001 $\underline{M}$ azide solution contained many golden flaky crystals, and the absorbance of the supernatant solution did not differ from that of the blank. Half molar solutions of sodium azide were effective for color development for at least two months after preparation.

Effect of pH. Figure 2 shows the effect on the color development, using 0.01 $\underline{M}$ azide, of varying the pH from 3.3 to 10.0. Hydrazoic acid is weak (pK = 4.72) and at low pH values the azide ion concentration is suppressed, giving low percents of maximum color development. At high pH values the palladium complex probably hydrolyzes, thus accounting for the suppression of color development. The phosphate buffer system was chosen because it has a high buffer capacity in the optimum pH region from 4.6 to 7.3.

Effects of Chloride and Phosphate. The tetrachloro palladium (II) complex, which has a dissociation constant of 6×10^{-14} (10), is well known, and both higher and lower chloro complexes have been reported (9). Phosphate apparently forms a highly dissociated complex with palladium, as shown by the following experiments. Palladium ion (as perchlorate) exhibits an absorbance peak at 380 mμ with a molar absorptivity of 86. The addition of phosphoric acid to 4×10^{-3} $\underline{M}$ palladium perchlorate in 0.5 $\underline{M}$ perchloric acid, holding the ionic strength at 1.0 with sodium perchlorate, causes shifts in the

absorbance.   An increase in absorptivity is observed in 0.01 $\underline{M}$ phosphoric

acid solution but the absorbance peak remains at 380 mµ.   A peak shift

becomes perceptible when the concentration of phosphate is increased to 0.1 $\underline{M}$,

and the peak shifts to near 390 mµ at a phosphate concentration of 0.5 $\underline{M}$, with

a corresponding molar absorptivity of 106.   These changes are shown in Fig. 3,

except for the 0.01 $\underline{M}$ phosphoric acid solution.

Although phosphate and chloride both form complexes with palladium (II),

phosphate does not interfere with the azide color development under the con-

ditions for analysis and chloride interferes only slightly.   With constant

concentrations of 2 p.p.m. palladium, 0.04 $\underline{M}$ azide and 0.6 $\underline{M}$ phosphate buffer,

at pH 6.5, the chloride concentration was varied from 0.016 $\underline{M}$ to 0.64 $\underline{M}$.   Up

to a chloride concentration of 0.08 $\underline{M}$ the absorbance was the same as in the

absence of chloride, but at, or above, 0.16 $\underline{M}$ chloride there was a constant

negative deviation of 3%.   The same absorbances were obtained in the absence

of phosphate, with the pH adjusted to the region of the plateau (Figure 2).

Gross variations in ionic strength thus have no effect on the absorbance.

EXTRACTION

Palladium was held at 100 µg. in all extraction studies except those

for determination of the extraction range.   Color intensity was obtained after

extraction and back-extraction, as described under the recommended procedure,

unless otherwise specified.

Effect of pH.   Figure 4 shows the effect of pH on extraction into n-

butyl alcohol when the volumes of aqueous and organic phases were 10 ml. each,

and the concentrations of azide and monosodium phosphate were 0.1 $\underline{M}$ and 0.5 $\underline{M}$,

respectively.   The pH was adjusted by dropwise addition of 85% phosphoric acid

or 10 $\underline{M}$ sodium hydroxide.   A similar curve was obtained when sodium sulfate and

sulfuric acid were used. The pH of the aqueous phase was obtained each time
after extraction and the absorbance values read either for the back-extracted
color, if more than 50% of the color was judged (visually) to be extracted,
or for the aqueous phase after neutralization, if less than 50% was extracted.

The absorbance maxima at 315 mμ, shown in Figure 1 for the n-butyl
alcohol extracts, indicate that the extracted species is the tetraazido com-
plex of palladium (2). The color intensity of the organic phase is very
sensitive to small pH changes in the aqueous phase. The yellow color appears
in the organic phase only between aqueous pH values of 2.0 and 2.7 and a change
of 0.44 pH units (pH 1.81 to 2.25) induces a difference of 24% in the ab-
sorbance values. For this reason it is not advisable to read the absorbance
of the n-butyl alcohol extract. Below pH 2.0 a red insoluble material appears
either as a colloid suspended in the alcohol phase or as a coagulated pre-
cipitate at the phase interface. This material, thought to be palladium
azide (2), in no way impairs the performance of the extraction and back-
extraction.

Effect of Azide. The azide concentration was varied from 10^{-1} to
10^{-4} M, with the monosodium phosphate held constant at 0.5 M. The pH was
adjusted below 2.7 with phosphoric acid and the volumes of aqueous and organic
phases were 10 ml. each, as above. Quantitative recovery of palladium was
found until the azide concentration dropped below 5×10^{-3} M. Below this value
some reduction of palladium occurred, as evidenced by the scattering of re-
sults and by the collection of a black powder at the phase interface in the
case of the 10^{-4} M azide.

Effect of Chloride. Chloride, unlike azide, is completely ionized at
at all acidities and, at low pH, is a very effective complexing agent for pal-
ladium. The chloropalladium complexes are not extracted into n-butyl alcohol.

To achieve quantitative recovery in the extraction step, chloride should be kept below 0.002 $\underline{M}$. For example, 90% extraction was found at 0.01 $\underline{M}$ chloride. This is the principle reason for displacement of volatile acids in the recommended procedure. The amount of chloride introduced with the dilute palladium stock for preparing the calibration curve is negligible.

Extraction Range and Volume Ratio. Quantitative recovery was achieved for 25-150 µg. palladium under the conditions in the recommended procedure and 96% recovery for 200 µg. The upper limit for quantitative extraction is well above the 115 µg. palladium which allows the optical absorbance to remain within the optimum range; hence, the extraction is not a limiting factor in the analysis. Again with the same solution conditions, the volume of n-butyl alcohol was held at 10 ml. and the volume of aqueous phase varied from 10 ml. to 50 ml.. Quantitative extraction was found up to a volume ratio of 3:1 aqueous to organic, but the recovery dropped rapidly beyond that point to 78% at a 5:1 volume ratio.

EFFECT OF FOREIGN IONS

The largest relative standard deviation shown in Table I was taken as a criterion to establish interference levels. The amounts of cations listed in Table II will not produce more than 2.3% error for 50 µg. (2p.p.m.) palladium. These cations were selected either because they are common impurities occurring with palladium or because they may be added as metals to reduce palladium in separations, and were tested in the valence state in which they would normally occur. Interference levels were determined in the case of the base metals by descending in 10 mg. steps from 50 mg. until an error of less than 2.3% was reached. Interference levels for the platinum metals

Table II.   Tolerance for Foreign Cations

Foreign cation	Max. mg. giving less than 2.3% error
Al[a]	10
Fe	>50
Co	10
Ni	40
Cu	20
Zn	>50
Ag[b]	<10
Cd	>50
Au	0.5
Pb[b]	<10
Ru	0.5
Rh	6.0
Os	0.8
Ir	1
Pt	<0.03

[a]With 0.2 $\underline{M}$ azide; not all Pd extracted with 0.1 $\underline{M}$ azide.

[b]Precipitate with azide carries 10-20% Pd.

were established by descending from 6 mg. in decimilligram amounts. Platinum

is extracted and back extracted with palladium and causes high results.

Silver and lead precipitate as azides and entrain 10-20% of the palladium.

Aluminum is evidently strongly complexed by azide and will caues low results

unless a ratio of at least 3:1 azide to aluminum is present, plus the con-

centration necessary for the palladium extraction. Fluoride does not prevent

this interference by aluminum. Methods are given in the literature for

isolating trace amounts of palladium from platinum, lead, and silver (5).

Some cations, such as some platinum metals and copper, follow palladium in

the extraction; however, the amounts extracting do not interfere in the sub-

sequent determination, except for platinum itself.

The interferences caused by chloride have been discussed. Inasmuch

as this anion must be removed by volatilization it was not deemed necessary to

test a large list of volatile anions. Nitrate absorbs strongly at 315 mμ but

presents no problem as it does not follow palladium in the extraction, even

if it were not removed by volatilization. Perchlorate causes no interference

and the other common non-volatile anions, sulfate and phosphate, are used in

the procedure.

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ACKNOWLEDGMENT

Figure 1. Absorption spectra of analytical species and reagents.

    ⬤ 5 p.p.m. Pd in n-BuOH; pH 2.25, aq. phase

    ◯ 5 p.p.m. Pd in n-BuOH; pH 1.81, aq. phase

    △ 2 p.p.m. Pd, back extracted, pH 6.5

    ◆ 1.0 $\underline{M}$ NaN$_3$

    ◇ 1.0 $\underline{M}$ phosphate

Figure 2. Effect of pH on color development.

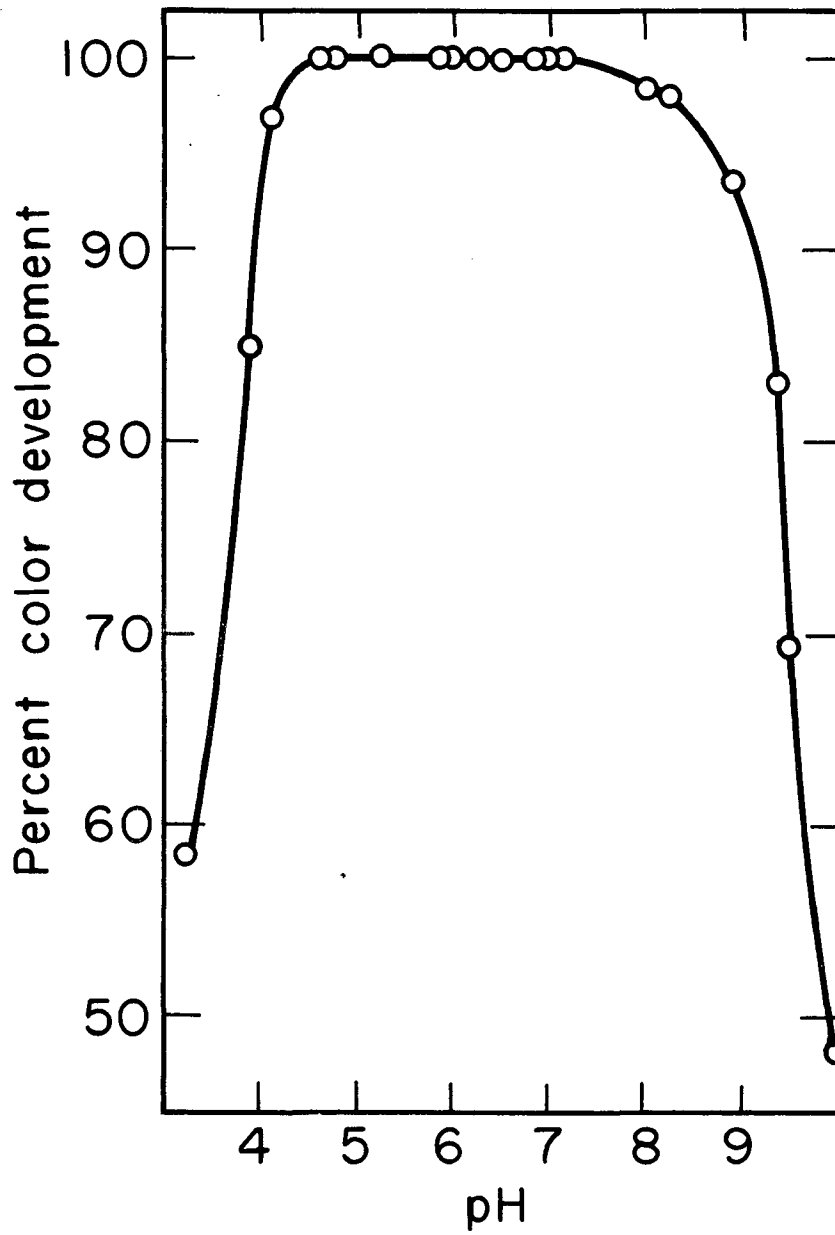Figure 3. Effect of phosphate on absorbance-wave length curves of 4×10^{-3} $\underline{M}$ Pd^{+2}.

    ◯ 0.5 $\underline{M}$ H$_3$PO$_4$

    ⬤ 0.1 $\underline{M}$ H$_3$PO$_4$

    △ 0.0 $\underline{M}$ H$_3$PO$_4$

Figure 4. Effect of pH on extraction with n-butyl alcohol.
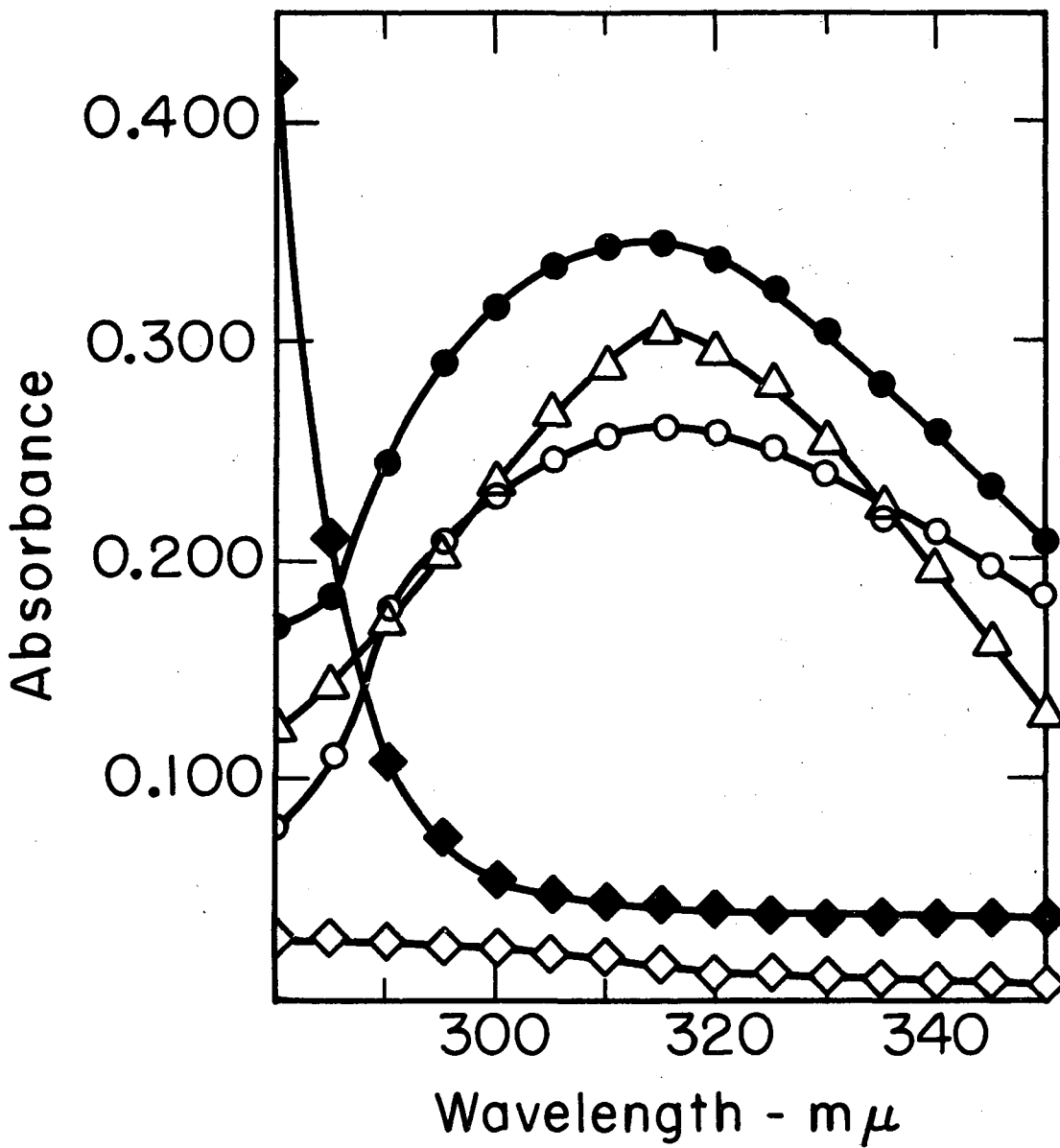
Fig. 1

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Fig. 2
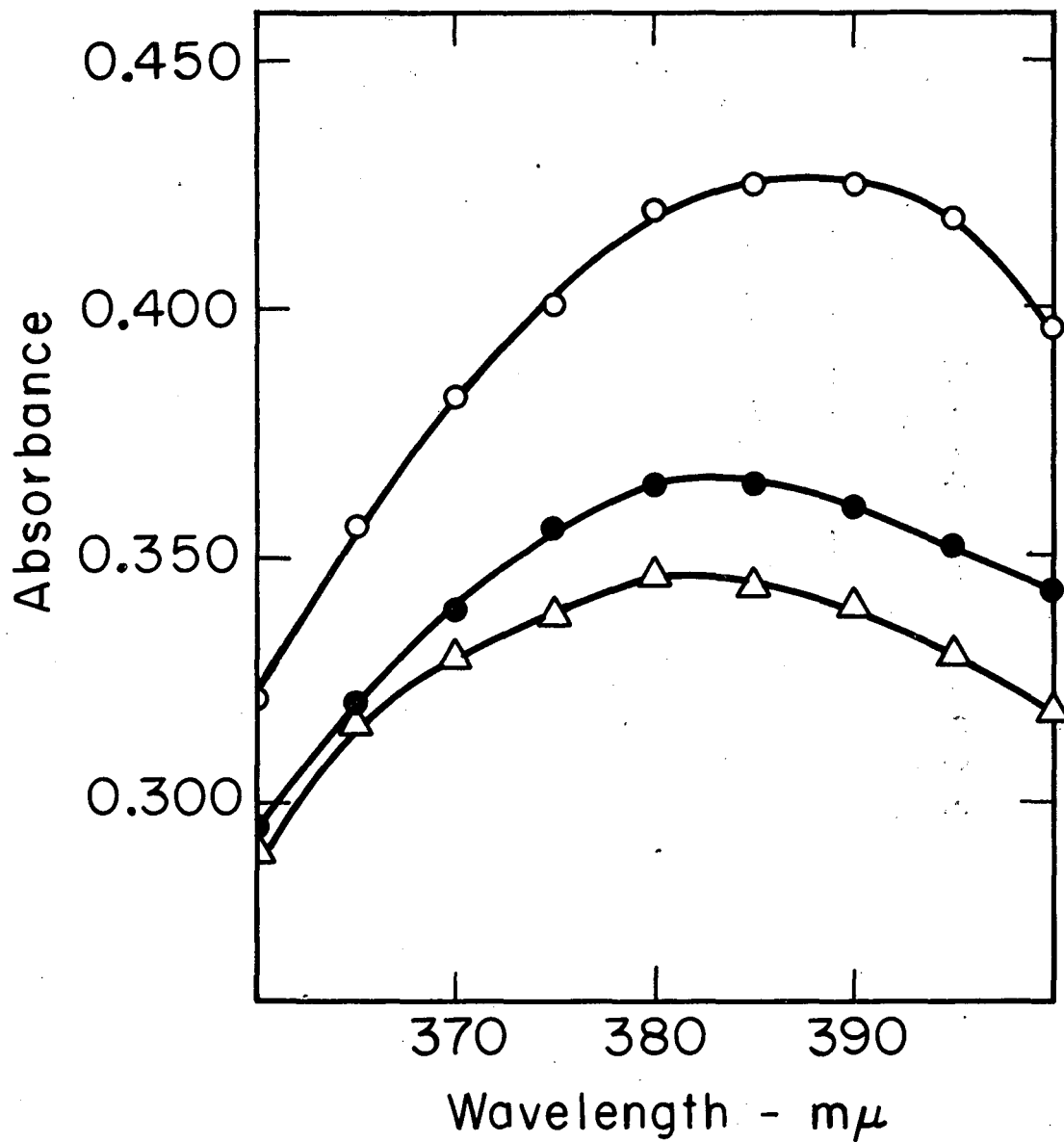
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Fig. 3

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Fig. 4