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ABSTRACT

The titration of palladium (II) by oxidation with hypochlorite to palladium (IV) is made feasible through the stabilizing influence of a 0.5 M chloride -0.05 M azide supporting electrolyte at pH2 to 3 on the palladium (IV) species, resulting in a marked reduction of the oxidation potential of the Pd(IV)/Pd(II) couple. The titration end point is detected with a rotated platinum electrode at 0.5 V versus a saturated calomel electrode. The method is most useful in the range (0.5-2.1 mg Pd) slightly above that covered by spectrophotometry and below that conveniently amenable to gravimetry, with a precision of about 0.5 percent. High ratios of common metals and platinum to palladium are tolerated. Deviations from the expected 2:1 hypochlorite to palladium ratio were found while developing the procedure; these deviations are of no consequence when the titrant is standardized against palladium. The effects of chloride concentration, azide concentration, pH, temperature, time of titration, photoreduction and concentration of palladium(IV) on the ratio were studied. Formal potential measurements of the Pd(IV)/Pd(II) couple in the recommended supporting electrolyte gave values from 0.64 to 0.53 V on changing the pH from 2 to 3, with an attendant 10-fold increase in azide ion concentration.

Although the principal oxidation states of palladium are 2+ and 4+, there has apparently been no analytical procedure reported for the oxidimetric determination of palladium(II). The lack of such a method is probably due to the fact that no medium has been found in which there is a favorable difference in the oxidation potentials of palladium and an oxidant. For example, in a chloride medium the potentials for the Pd(IV)/Pd(II) and Ce(IV)/Ce(III) couples are about the same(1,2), and permanganate cannot be used because it readily oxidizes chloride.

The method presented here utilizes, for the first time, the oxidation of palladium(II) to Palladium(IV) with hypochlorite. This titration is made feasible through the stabilizing influence of the chloride-azide supporting electrolyte at pH 2 to 3 on the palladium(IV) species, resulting in a marked reduction of the oxidation potential of the Pd(IV)/Pd(II) couple. The titration end point is detected with a rotated platinum electrode (RPE) at 0.5 V versus a saturated calomel electrode (SCE). Fairly small quantities of palladium(II) can be titrated with a precision of about 0.5 percent. Large amounts of diverse metal ions and oxygen can be tolerated and few substances give interfering waves. Additional advantages are that readily available inorganic reagents are used and that azide can be easily removed prior to the determination of other constituents.

EXPERIMENTAL

Apparatus and Reagents. Polarograms were obtained with a Leeds and Northrup Electrochemograph, Type E. The electrodes used were a Lingane type saturated calomel electrode (3) and an electrode having a 3 mm length of 0.5 mm diameter platinum wire exposed (4), and rotated at 600 rpm by a synchronous motor. Polarograms presented in Figures 1 and 3 were obtained using a recommended electrode pretreatment (5). The pH measurements were made with a Beckman Model 76 expanded scale pH meter. Potential measurements were made with a DigiTec digital DC voltmeter which was checked frequently against a Leeds and Northrup Potentiometer (Cat. No. 8691).

A stock solution containing 0.525 mg of palladium per milliliter was prepared as previously described (6). Sodium azide having a purity of 99.2%, as determined from the hydrogen ion consumed an oxidation with nitrite (7), was used to make a 1.00M solution. Solutions approximately 0.1M in hypochlorite were prepared by diluting reagent grade 5% sodium hypochlorite and were stored in amber glass stoppered bottles. They were standardized every three or four days by the iodine-thiosulfate method. Hypochlorite solutions are moderately stable; for example, over a 30 day period a solution decreased in strength from 0.0981 to 0.0970M. A diluted solution (0.01M) was prepared fresh daily. Solutions of other chemicals were prepared from reagent grade materials. The metals used in the interference tests were in the form of either chlorides or perchlorates.

Preliminary Tests. Polarograms of acidified chloride-azide solutions, at positive potentials versus the SCE, were found to give a cathodic wave for hypochlorite but not for palladium(II). Furthermore, the hypochlorite wave disappeared when excess palladium(II) was added. This observation is the basis of the method presented.

Formal Potential Measurements. The formal potential measurements were made in two ways, employing the conditions described in the recommended procedure and at a constant temperature of 25.0° ± 0.1°C. In one method a known amount of palladium(II) was oxidized with a small excess of hypochlorite and the palladium(IV) allowed to undergo slow photoreduction. The changing potential was correlated with the ratio of oxidized to reduced palladium and the formal potential determined at a ratio of 1:1. The ratios were found by determining the palladium(IV) content spectrophotometrically at 380 mμ, a wavelength at which the Pd(IV)/Pd(II) absorbtivity ratio is 21.8:1.

In the second method, samples containing 1.050 mg of palladium(II) were one-half titrated, the electrodes were inserted and the beakers covered with Parafilm to minimize loss of volatile hydrazoic acid. The potential was allowed to drift until it did not vary by more than one mV in 10 minutes (about one hour); the solution was then titrated for palladium(II) and the formal potential calculated. The pH was measured at the beginning and at the end of each run.

Recommended Procedure. Standardize the hypochlorite solution in the following manner. Aliquot from 0.5 to 2.1 mg of standard palladium(II) into 150 ml beakers, add 10 ml of a 5.00M sodium chloride solution and 5 ml of a 1.00M sodium azide solution, and dilute to 100 ml with water. Adjust the pH to between 2 and 3 with perchloric acid. Insert the salt bridge and the RPE, which has been immersed in 1:1 nitric acid and rinsed in water, and polarize at 0.5V vs. SCE. After the initial charging current decay titrate, while stirring magnetically, with 0.01M sodium hypochlorite from a 5 ml semimicroburet. Continue the titration for at least 1 ml past the end point in 0.2 ml intervals. Record and plot the current versus milliliters of titrant to obtain the end point.

The sample is dissolved in a minimum of aqua regia, nitric acid, hydrochloric acid or perchloric acid. Nitric acid is a good prior oxidant for low valent ions (e.g., Fe^{2+}) which react with hypochlorite. If either of the first two solvents are used, displace them with hydrochloric acid and, finally, remove most of the chloride by evaporating nearly to dryness. Titrate the sample, containing only tolerated ions (Table II), for palladium(II) as described above.

DISCUSSION

The hexachloropalladium(IV) ion is reported to be formed when palladium is dissolved in aqua regia, or when a palladium(II) chloride solution is saturated with chlorine gas. Its alkali metal or ammonium salts react with hot water to generate chlorine, and with aqueous ammonia to liberate nitrogen (8). Latimer gives a standard oxidation potential of 1.288 V for the Pd(IV)/Pd(II) couple in a chloride medium (1).

From the foregoing, one would not expect oxidimetry to be a fruitful method for determining palladium(II) unless the oxidation potential of the palladium couple could be lowered considerably. This would be possible provided that a complexing agent having a greater affinity for the palladium(IV) ion than for the palladium(II) ion could be found. The chloride-azide supporting electrolyte for palladium satisfies this requirement. In a preceding paper (6), the effect of pH on the ability of azide to complex palladium(II) is clearly shown. At pH values less than 4.6 the amount of the tetraazido complex formed decreases rapidly. In contradistinction, azide must strongly complex the four valent species as shown by the characteristic color deepening evident during the titration at pH values as low as 1.5, where the hydrazoic acid is largely molecular and chloride ion, another complexing agent, is present in great excess. The species present during the titration is not known, but the existence of mixed chloride-azide complexes is indicated by the dependence of the color intensity, as measured spectrophotometrically, on the chloride, azide and acid concentrations. The titration is not feasible in the absence of azide.

Figure 1 shows polarographic scans of the supporting electrolyte (SE), SE plus palladium(II), and SE plus hypochlorite. The current shown at 0.5 V vs. SCE for the hypochlorite wave is approximately 0.7 μA using a "clean electrode" (5) and a scan rate of 3.3 mV/sec. Under the conditions employed in the titration procedure, using a constant potential of 0.5 V vs. SCE, the final current obtained is about ten times as great.

Deviations from the expected ratio of 2:1 hypochlorite to palladium were found while developing the recommended procedure. The effects of the following variables on this ratio were studied: chloride concentration, azide concentration, pH, temperature, time of titration, photoreduction of palladium(IV) and concentration of palladium. Two studies were made in which azide was held constant at the 0.1M and 0.05M levels and the chloride concentration was varied. In both studies 0.525 mg of palladium was titrated with 0.01M hypochlorite at pH 2. At the 0.1M azide level the results were generally high by 6% or more when the chloride concentration was above 0.05M. Below 0.05M chloride, instability in the current beyond the end point was encountered. When the azide concentration was held at 0.05M, the current past the end point was stable and the ratio of hypochlorite to palladium was 2.06 ± 0.01 (std.

dev.) in the chloride concentration range from 0.3 to 0.8M. The current stability decreases both above and below these chloride levels.

At a constant chloride level of 0.5M, and at pH 2, azide can be varied from 0.1 to 0.03 M without affecting the ratio of 2.06, but below the 0.03M level the current stability suffers and the ratio increases.

The effect of pH on the titration was studied under the conditions described in the recommended procedure, holding the palladium(II) constant at 0.525 mg. Although the ratios vary but little (2.06 ± 0.02) between pH 1.5 and 4.0, the slopes of the titration curves do vary, as shown in Figure 2. The formal oxidation potential of the Pd(IV)/Pd(II) couple increases with decreasing pH, as discussed below. It is reasonable to assume that at pH 1.5 the palladium(IV) is being reduced at the RPE, thus accounting for the positive slope prior to the end point. At pH values less than 2.0 the current, after each addition of titrant, decays slowly to a constant value. This may be due to a slower rate of oxidation of palladium. These factors combine to lessen the feasibility of titrating at pH values much lower than 1.5. To explain the bowing of the titration curve after the end point at pH 4.0, it is necessary to consider the rate of decay of current due to reduction of hypochlorite by azide at various acidities. The half lives for the pseudo first order reactions are 1410 and 528 seconds at pH 2.19 and 3.03, respectively. At pH 4.10 the half life is 73 seconds and between pH 5 and 8 it is about 30 seconds; at pH 9.11 it increases to 109 seconds. This behavior indicates that the reaction is between azide ions ($pK_{HN_3} = 4.72$) and hypochlorous acid molecules ($pK_{HClO} = 7.50$).

Temperature does not affect the ratio; samples titrated at 23°C and at 2°C gave the same values. The current response past the end point, however, was about three times as great at 23°C as at 2°C.

Titrating 0.525 mg of palladium, using 0.2 ml intervals, requires 3 minutes or less, since a steady current is reached in a few seconds after each addition of titrant. Addition of the titrant at 30 second intervals extended the titration time to 5 minutes but did not effect the titer. Addition of the titrant at one minute intervals (total time 10 minutes) again did not affect the titer, but the titration curve was slightly bowed beyond the end point.

When 0.053, 0.105, and 0.158 mg of palladium were titrated with 0.001M hypochlorite, using the recommended conditions, ratios of 2.38, 2.30 and 2.26 were obtained, respectively. The current stability in this range was poor. Values from 2.05 to 2.08 were obtained in the range from 0.5 mg to 2.1 mg of palladium using 0.01M hypochlorite, and ratios of 1.96, 1.96, and 1.95 were obtained on titrating 5.25, 10.50, and 15.75 mg of palladium with 0.1 M hypochlorite. The current stability was good from 0.5 mg to 16 mg of palladium, but above 16 mg, the current was not stable. This may be due to lack of sufficient azide to complex the palladium(IV) produced.

Oxidized solutions of palladium were observed to lose their characteristic reddish-brown color slowly, on standing, with an attendant formation of gas bubbles. In view of the fact that the ratios obtained were greater than 2:1 over the palladium weight range from 0.05 to 2.1 mg, the possibility of photo-induced reduction of palladium(IV) was investigated. Solutions of completely oxidized palladium were subjected to the light in the work area and were periodically examined spectrophotometrically at 380 mμ to determine the palladium(IV) content. Initial reduction rates of 1% and 5% per minute were obtained at the 0.5 mg and 0.05 mg palladium levels, respectively. Palladium(IV) did not undergo such reduction in the dark. This suggests that it might be possible to develop a titration method in a suitable light, perhaps red, without such reduction and consequently with the expected ratio of 2:1 hypochlorite to palladium.

The marked ability of azide ion to complex palladium(IV) is illustrated by the formal potential measurements shown in Table I.

Table I

Formal Potential Variation with pH in 0.5<u>M</u> Chloride and 0.05<u>M</u> Azide

pH	$E^{o'}$
2.05	0.64
2.21	0.59
2.60	0.55
2.73	0.54
3.20	0.53

$E^{o} = 1.288 (Cl^{-}$ medium)

The azide ion concentration increases by one order of magnitude on the pH interval from 2 to 3, with a corresponding decrease of 0.11 V in the oxidation potential. The results obtained by the two methods agree within 10 to 15 mV. In the first method the beaker was continually exposed to air and samples were periodically withdrawn for analysis, thus entailing loss of hydrazoic acid. This loss increased the pH and decreased the azide concentration throughout the experiment. Both factors effect the oxidation potential and thus reduce the precision obtainable. The results given in Table I were obtained using the second procedure, where loss of hydrazoic acid was minimized.

Table II shows the recovery of 0.525 mg of palladium in the presence of large amounts of diverse ions. The cation interferences giving waves at potentials greater than 0.0 V vs. SCE in the supporting electrolyte are shown in Figure 3. The interference study was begun around the 100 mg level of diverse ion and, if interference was encountered, the diverse ion content was decreased in 10 mg steps until the error obtained was less than 3%. The diverse ions selected were those of the precious metals group and some base metals apt to accompany palladium as common impurities or to be used as a metal for reduction. More than 20 mg of gold or 30 mg of rhodium(III) give high results. By polarographic comparison (Fig. 1 and Fig. 3), iridium(IV) is as strong an oxidizing agent as is hypochlorite and both oxidants are capable of oxidizing palladium(II) in the recommended supporting electrolyte, as verified by the result shown in Table II.

The potential selected is sufficiently positive that most of the possible interfering ions do not give waves, yet sufficiently negative that the excess hypochlorite is sensitively detected. Although palladium alone can be titrated with an error of less than 1%, the 3% criterion for interference was chosen because it is about the error level encountered in either the spectrophotometric method or the gravimetric method for the weight range selected. The conditions selected for the recommended procedure are about midway of the optimum chloride and azide concentration ranges. The chloride concentration used also aids in keeping lead in solution, an advantage if the

Table II

Tolerance for Foreign Ions
(0.525 mg Pd in each)

Foreign ion	mg added	mg Pd found (Av. duplicates)	% error
Cr^{3+}	100	0.512	-2.5
Fe^{3+}	100	0.527	+0.4
Co^{2+}	111	0.515	-1.9
Ni^{2+}	116	0.526	+0.2
Cu^{2+}	103	0.510	-2.9
Zn^{2+}	108	0.530	+1.0
Rh^{3+}	30	0.532	+1.3
Ir^{4+}	2	0	-100
Pt^{4+}	118	0.526	+0.2
Au^{3+}	20	0.526	+0.2
Pb^{2+}	108	0.511	-2.7
Na_2SO_4	1,000	0.521	-0.8
$NaNO_3$	1,000	0.518	-1.5

palladium has been collected in a lead button by fire assay. The pH interval between 2.0 and 3.0 gives an optimum current response with respect to time and stability and is sufficient to prevent hydrolysis of many heavy metal ions.

The range between 0.5 mg and 2.1 mg of palladium was selected because the current stability is good, the variation in the ratio of hypochlorite to palladium is small and large ratios of diverse ions to palladium are tolerated. Also, this range is slightly above that covered by spectrophotometry and below that conveniently amenable to gravimetry. To estimate the precision of the recommended procedure, eight titrations were made. An average ratio of 2.06:1 was obtained, with a standard deviation of ±0.01 and a range from 2.05 to 2.08.

Cerate, permanganate and dichromate cannot be used as oxidants in place of hypochlorite. The first two reagents quantitatively oxidize azide to nitrogen in acid solution, and dichromate does not appear to oxidize palladium (II) in the chloride-azide medium.

LITERATURE CITED

(1) W. M. Latimer, "Oxidation Potentials," 2nd ed., Prentice-Hall, Englewood Cliffs, N. J., 1952, p. 203.

(2) G. F. Smith, "Cerate Oxidimetry," G. Frederick Smith Chemical Co., Columbus, Ohio, 1942, p. 22.

(3) J. J. Lingane, "Electroanalytical Chemistry," 2nd ed., Interscience, New York, 1958, p. 362.

(4) J. T. Stock, "Amperometric Titrations," Interscience, New York, 1965, p. 102, fig. a.

(5) I. M. Kolthoff and N. Tanaka, Anal. Chem., 26, 632 (1954).

(6) R. G. Clem and E. H. Huffman, Ibid, 37, 86 (1965).

(7) Ibid, 37, 366 (1965).

(8) A. F. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed., Interscience, New York, 1966, p. 1035.

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FIGURE CAPTIONS

Fig. 1. Polarograms of supporting electrolyte (SE) and reactants.

Fig. 2. Amperometric titration of palladium(II) with 9.61×10^{-3} $\underline{M}$ hypochlorite at various pH values.

Fig. 3. Polarograms of diverse ions giving waves at positive potentials.

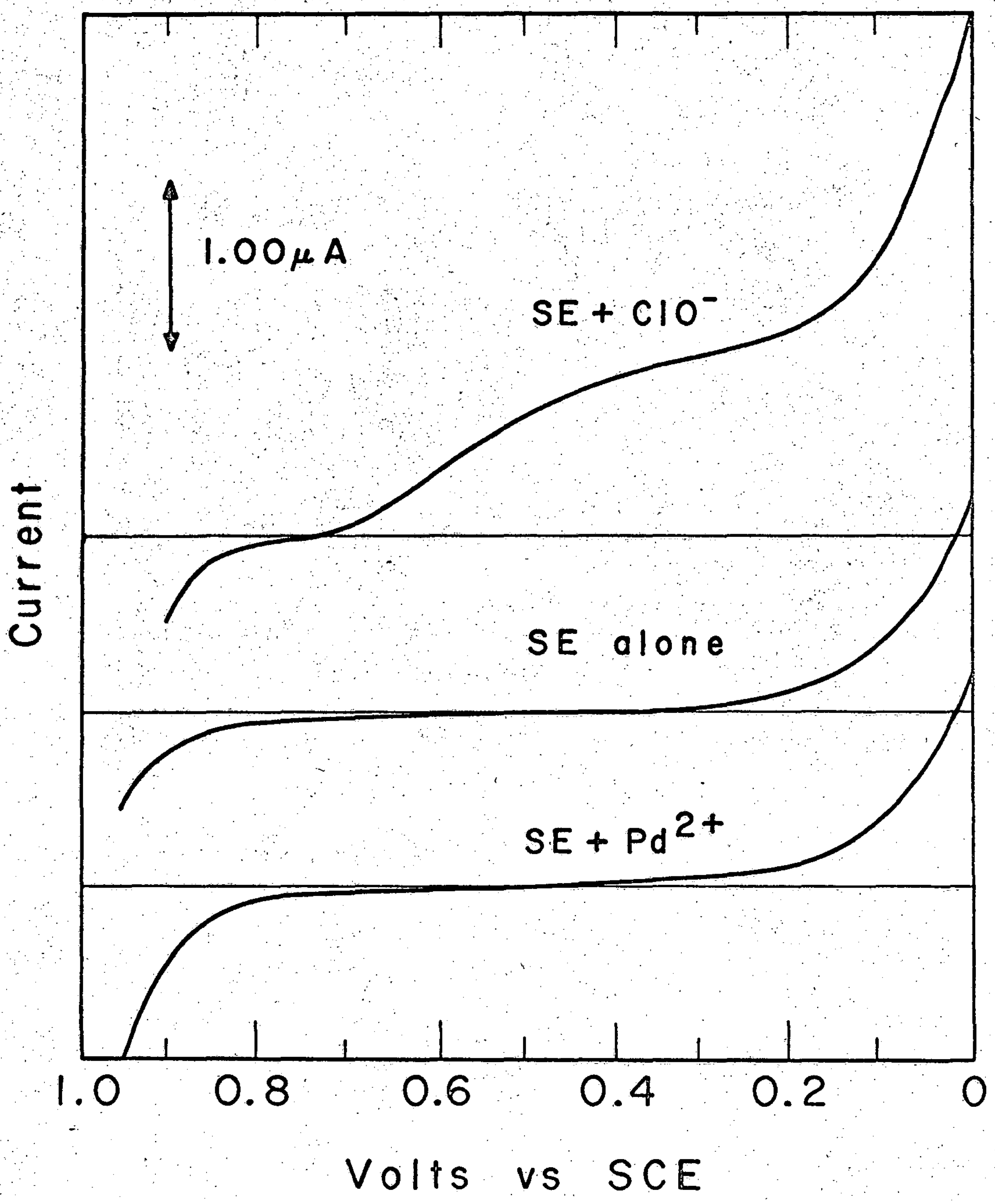

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Fig. 1

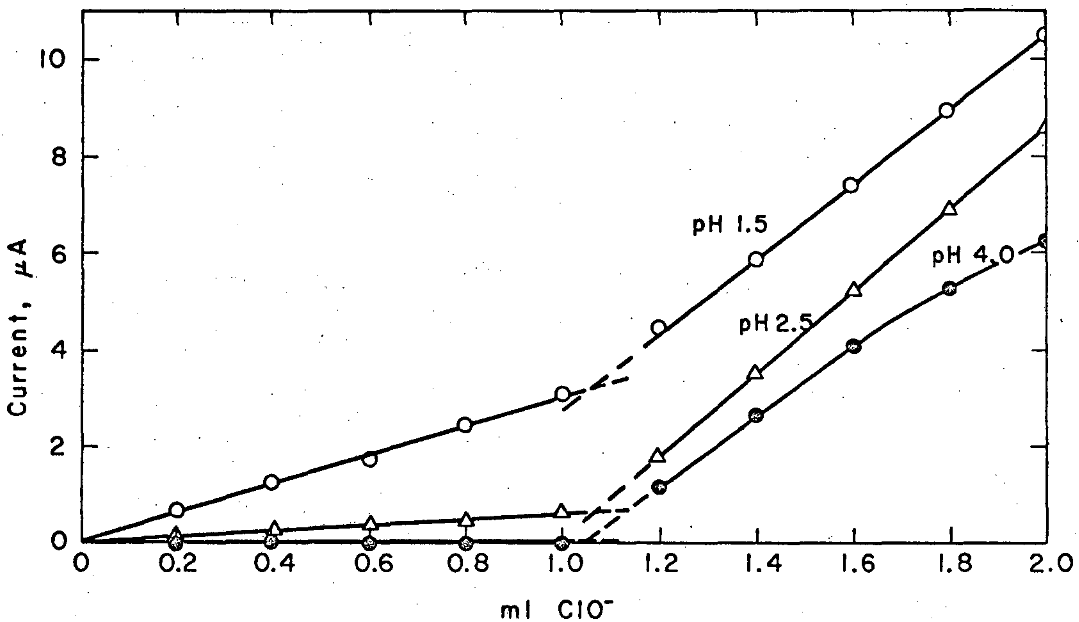

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Fig. 2

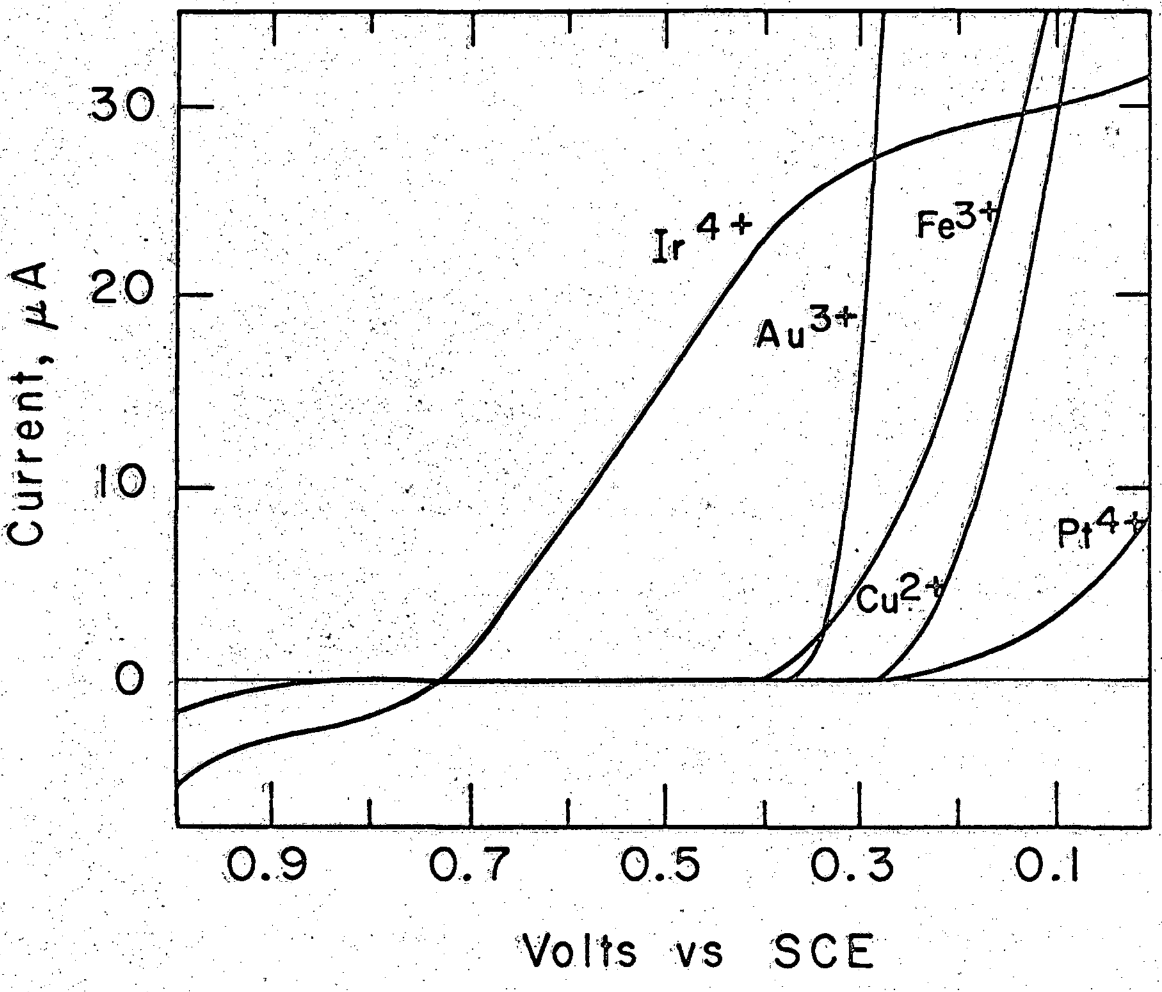

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Fig. 3