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Direct Polarographic Determination of Metal Ions after Extraction with Oxine in 1-Butanol

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A direct extraction-polarographic method has been investigated with several metal ions extracted into 1-butanol. Oxinates of cadmium, cobalt, and iron were quantitatively extracted with 0.1*M* oxine in 1-butanol in the pH range of 5.1 – 8.0, 3.9 – 7.0, and 2.7 – 4.8, respectively. The polarograms were recorded in 0.1*M* lithium perchlorate as the supporting electrolyte. Under the given conditions these metal oxinates give well defined waves with $E_{1/2}$ of −0.62 volt versus SCE for Cd, −0.24 volt for Co, and −0.23 volt for Fe, respectively. In the case of equal volumes of the two phases the relation between the limiting current and the concentration of metal ions in the aqueous solution was found to be linear in the range of $10^{-5}M$–$2.5\times10^{-4}M$ with all the metal ions examined. In the differential pulse polarographic analysis the calibration curve of cadmium was linear in a range of $7.5\times10^{-8}M$–$2.5\times10^{-6}M$, where the volume ratio of the organic phase to the aqueous one was 1:1 before extraction.

INTRODUCTION

Solvent extraction of metal chelates is perhaps the most effective of all separation methods. Particularly in the colorimetric determination of trace elements it has an extremely wide range of application because of its simplicity and speed. Aside from the spectrophotometric method, however, the polarographic determination of an organic phase following solvent extraction is limited to organic solvents with a high dielectric constant. This is mainly because most of the water-immiscible organic solvents, *e.g.*, benzene or chloroform for the extraction of metal complexes, have low solubility of the supporting electrolyte.

The extraction polarographic method is the application of two techniques, *e.g.*, solvent extraction and polarographic determination for analytical purpose. This technique may be achieved in six ways: (a) destruction of the organic material in the extract and polarographic analysis of the residue;[1] (b) re-extraction of the organic constituent into the aqueous phase, which is presented for the polarographic electrolysis;[1] (c) use of the homogeneous ternary mixture of solvents, *e.g.*, solution of an aqueous hydrochloric acid solution and methylcellosolve added to the chloroform extract, and polarographic analysis;[2] (d) addition of the supporting electrolyte–methanol solution to the organic phase and polarographic examination;[3] (e) dissolution of the solidified extract in non-aqueous solvent containing the supporting electrolyte after extraction with molten solid solvent and polarographic determination;[4] (f) direct polarographic determination of the organic phase.[5]

One of the authors (T. Fujinaga) has published the papers on the extraction

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polarographic analyses[2,4] and on the polarographic studies in non-aqueous solvents.[6] On the basis of these results this paper deals with a direct polarographic determination of metal oxinates by the direct addition of a supporting electrolyte after extraction of traces of cadmium, cobalt, and iron with the 8-hydroxyquinoline(oxine) 1-butanol solution. And a differential pulse polarographic estimation was applied to the low concentration (2.5×10^{-6} — $7.5\times10^{-8}M$) of cadmium ion.

EXPERIMENTAL

Reagents. $10^{-3}M$ standard solutions of cadmium acetate, cobaltous nitrate, and ferric ammonium sulfate were prepared and standardized by the conventional methods. $0.5M$ solution of lithium perchlorate was prepared by dissolving the anhydrous reagent grade material in 1-butanol. Oxine was purified twice by a steam distillation followed by a double crystallization from ethanol-water, and dissolved in 1-butanol to give a $0.1M$ solution. Reagent grade of 1-butanol was purified by a method similar to that used by Jones and Christian.[7] The water content of the solvent, as determined by Karl Fischer titration, was less than 0.01 %W. 1-Butanol has some suitable physical properties as is shown in Table I. Metal oxinates were prepared under the conditions described by Hollingshead[8]

Table I. Physical Properties of 1-Butanol[9]

freezing point	−88.62°C
boiling point	117.66°C (760 mm Hg)
vapor pressure	6.18 mm Hg (25°C)
density	0.8097 g/m*l* (20°C)
coefficient of viscosity	3.379 cp (15°C)
refractive index	1.3993 (20°C)
dielectric constant	17.51 DU (25°C)
specific conductance	9.12×10^{-9} mho/cm
solubility in water	7.45% W (25°C)
solubility of water	20.5% W(25°C)

Apparatus. A Yanaco Polarograph, Model p8, and a Princeton Applied Research Polarographic Analyzer, Model 174, with three electrode system were used with the dropping mercury electrode. A saturated calomel electrode was used as the reference electrode and connected to one compartment of the cell through potassium chloride-agar bridge. A spiral platinum electrode was used as the counter electrode, An H-type cell with a fine porosity of a sintered glass disc between the two compartments was used. Unless otherwise stated the following operating conditions were used; rate of potential sweep 0.2 V/min, drop time 4.60 sec, flow rate 2.12 mg/sec, and the height of the mercury head 60 cm with open circuit. Preliminary tests showed that there was no reproducibility when the experiments were carried out at the temperature of 25°C. So all the procedures were carried out at 15±0.5°C to suppress the decomposition of metal oxinates. The working solution

was thoroughly deoxygenated. The Hitachi-Horiba pH meter, Model M-5, with a glass electrode was used for measuring the pH values.

Extraction Procedure. An aliquot of metal ion solution was taken in a 50 m*l* sample tube, to this solution added 10 m*l* of the buffer solution adjusted ionic strength 0.2 with sodium perchlorate, diluted to 20 m*l* with distilled water, added 20 m*l* of 0.1*M* oxine 1-butanol solution, and thermostated in the water-bath at a temperature of 15±0.5°C. The aqueous and organic phases were not mutually presaturated before mixing. The sample tube was taken out from the thermostat maintained at 15±0.5°C and shaken for about 1 minute. In the water-bath, the tube was shaken two more times for about 1 minute, and the two phases were allowed to separate. The organic phase was then transferred to the mark of a 20 m*l* volumetric flask containing 4 m*l* of anhydrous 0.5*M* lithium perchlorate in 1-butanol. 10 m*l* of this solution was taken in the polarographic cell, deoxygenated for 20 minutes, and the polarogram recorded over the available potential range.

RESULTS AND DISCUSSION

(A) DC Polarography of Metal Oxinates

Polarograms of Metal Oxinates after Extraction. Preliminary experiments indicate that the supporting electrolytes soluble in 1-butanol, such as lithium perchlorate, lithium chloride, sodium perchlorate, and sodium chloride, can be used for the determination of metal ions. But the other salts, such as potassium perchlorate, ammonium perchlorate, and tetraalkylammonium salts, were not dissolved into 1-butanol to the 0.1*M* solution. With 0.1*M* lithium perchlorate as a supporting electrolyte, the metal oxinate solutions extracted from $10^{-4}M$ aqueous solutions exhibited well defined waves with $E_{1/2}$ −0.62 volt *vs.* aqueous SCE for Cd, −0.24 volt for Co, and −0.23 volt for Fe, respectively. In 1-butanol the extraction reagent oxine itself is reduced at −1.47 volt *vs.* aqueous SCE. The short underlines are galva-zeros. The results were summerized in Fig. 1 and Table II.

As is shown in Fig. 2 polarograms of cupric, bismuth, molybdenum, and plumbous oxinates have maxima in this supporting electrolyte. It was difficult to suppress them by the addition of maximum suppressor, *e,g.*, polyacrylamide or camphor. And the calibration curves of these metal ions were not linear.

Table II. Polarographic Data of Metal Ions

	Metal oxinates in 1-butanol			Metal ions in water (oxalate, pH∼4)[10]
	$E_{1/2}$ V *vs.* SCE	$i_d/C\,m^{2/3}t^{1/6}$ μA/m*M* mg$^{2/3}$ sec$^{-1/2}$	slope of log plot mV	$E_{1/2}$ V *vs.* SCE
Cd^{2+}	−0.62	0.72	30	−0.63
Co^{2+}	−0.24	0.40	60	>0*
Fe^{3+}	−0.23	0.41	65	−0.23

* 1 *F* K_2Ox, 0.2 F HOAc, 0.2 *F* NH_4OAc, for Co(III)→Co(II)

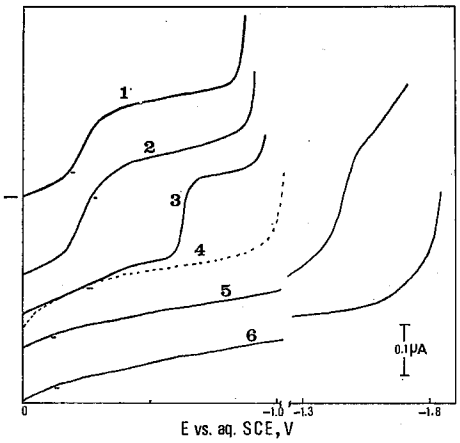

Fig. 1. Polarograms of $10^{-4}M$ metal oxinates after extraction with 1-butanol.
1) Fe(III)-oxinate (pH 3.8),
2) Co(II)-oxinate (pH 4.9),
3) Cd(II)-oxinate (pH 5.6),
4) blank solution (pH 5.6),
5) $2.0\times10^{-4}M$ oxine in 1-butanol,
6) $0.1M$ $LiClO_4$ in 1-butanol

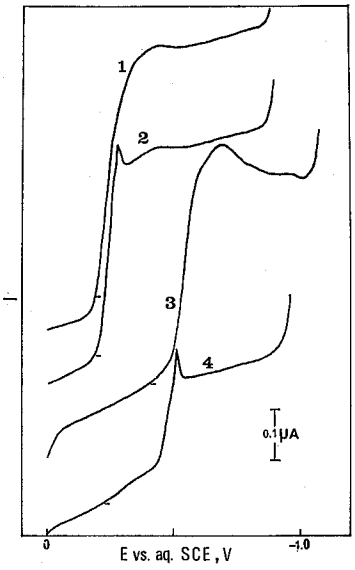

Fig. 2. Polarograms of metal oxinates after extraction with 1-butanol.
1) $2.0\times10^{-4}M$ Cu(II)-oxinate (pH 4.4_2),
2) $10^{-4}M$ Bi(III)-oxinate (pH 4.4_0),
3) $10^{-4}M$ Mo(VI)-oxinate (pH 2.4_5),
4) $10^{-4}M$ Pb(II)-oxinate (pH 5.7_5)

Because of the light absorption of oxine itself (310 nm) it will be also difficult to determine these metal ions with $0.1M$ oxine 1-butanol solution by spectrophotometry, except iron (680 nm).

Effect of pH and Reagent Concentration on Extraction of Metal Ions. Extractions were carried out by taking $10^{-4}M$ metal ions and $0.1M$ solutions of the reagent at the different pH. It was found that the extractions are completed in the pH ranges of 5.1–8.0 for Cd, 3.9–7.0 for Co, and 2.7–4.8 for Fe, respectively. The effect of pH on the extractabilities of metal ions is shown in Fig. 3. The optimum pHs of the aqueous phases after equilibration were chosen as 5.6 for Cd, 4.9 for Co, and 3.8 for Fe, respectively.[11]

And extractions were carried out at a constant pH for $10^{-4}M$ cadmium, equal volumes of 1-butanol and of the aqueous solution, and with the different concentration of the reagent. It was found that the extraction is quantitative (over 99%) down to $0.07M$ of the reagent, therefore in all cases the extractions were carried out with $0.1M$ of the reagent oxine.[12] This was identified by analyzing the aqueous solutions by atomic absorption spectrometry.

Effect of Height of Mercury Column on Limiting Current. The linear dependence of the limiting current on the square root of the height of mercury column indicate that the rates of reduction of metal ions are diffusion controlled (Fig. 4).

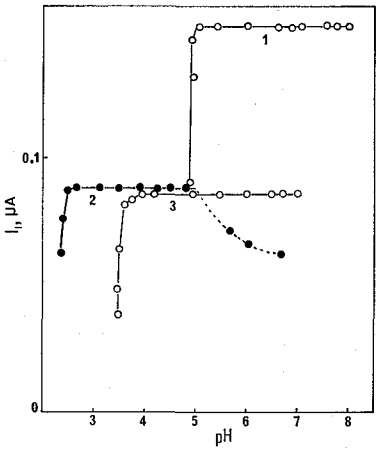

Fig. 3. Effect of pH on extractions of $10^{-4}M$ metal ions.
1) Cd(II), 2) Fe(III), 3) Co(II)

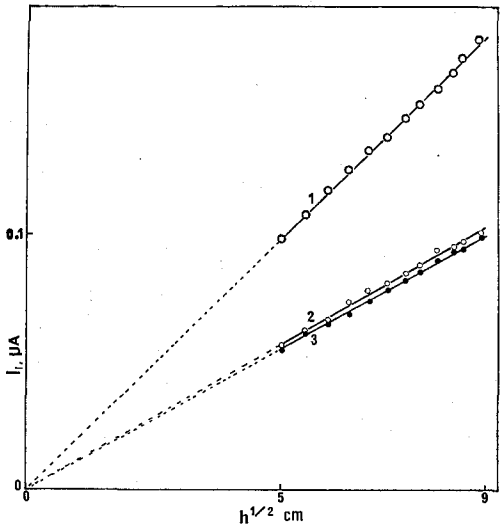

Fig. 4. Relation between height of mercury head and limiting current.
1) Cd(II), 2) Fe(III), 3) Co(II)

Electrocapillary curve. Figure 5 shows the electrocapillary curve obtained in $0.1M$ lithium perchlorate as the base electrolyte. The drop time was slightly longer in the presence of metal oxinate than that in the absence. The electrocapillary maximum in $0.1M$ $LiClO_4$ was found at -0.43 volt *vs.* aqueous SCE. Any metal oxinate in a concentration of $10^{-4}M$ was not electrocapillary-active in the DME.

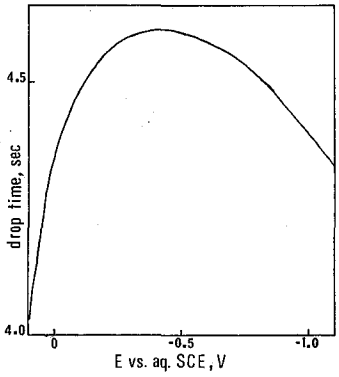

Fig. 5. Effect of potential on drop time in $0.1M$ $LiClO_4$ 1-butanol.

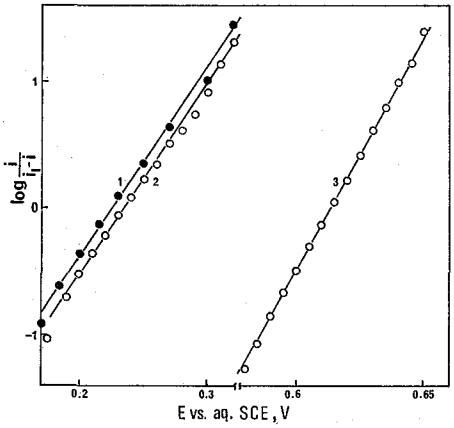

Fig. 6. Log plot analyses of metal oxinates.
1) Fe(III), 2) Co(II), 3) Cd(II)

Log-Plot Analyses of Metal Oxinates. The plots of log $i/(i_d-i)$ versus E gave straight lines with slopes of 30 mV for Cd, 60 mV for Co, and 65 mV for Fe, respectively (Fig. 6). These mean that metal oxinates irreversibly reduced slightly. These results indicate that cadmium oxinate is reduced with two electron change,

and ferric oxinate is reduced with one electron transfer. From the Fig. 1 and Fig. 6 it will be shown that cobalt has a mixture wave of oxidation and reduction. This was identified by the polarograms of pure cobaltic oxinate and cobaltous one.

Calibration Curves of Metal Ions. After extraction a number of polarograms were recorded in 1-butanol with the different concentrations of metal oxinate solutions. Diffusion currents are proportional to these metal oxinates in the range of $1.0\times10^{-5}M$ to $2.5\times10^{-4}M$. The aqueous phases after extraction with 1-butanol were analyzed by atomic absorption spectroscopy. Their results reveal that the extractabilities of cadmium are 98.8% for $7/4\times10^{-4}M$, 99.0% for $5/4\times10^{-4}M$, 99.5% for $6.0\times10^{-5}M$, and 99.8% for $3.0\times10^{-5}M$ of aqueous cadmium solution. As is shown in Fig. 7 these facts indicate that the waves of metal oxinates can be used for their quantitative determination under the conditions described above. The diffusion current constants ($i_d/Cm^{2/3}t^{1/6}$) calculated for the Ilkovič equation were 0.72 for Cd, 0.41 for Fe, and 0.40 for Co, respectively.

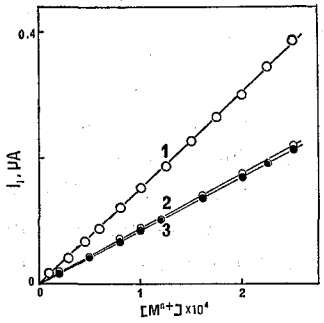

Fig. 7. Calibration curves of metal ions.
1) Cd(II), 2) Fe(III), 3) Co(II)

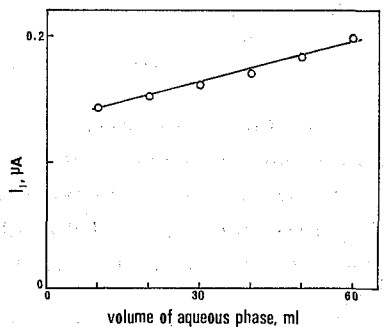

Fig. 8. Effect of volume of aqueous solution on limiting current of Cd(II)-oxinate in 1-butanol.

Effect of Volume of Aqueous Solution of Cadmium Oxinate. Polarograms were recorded in $0.1M$ lithium perchlorate after extraction with 20 ml of $0.1M$ oxine 1-butanol solution at a constant pH of 5.6, and the volume of the aqueous phase was varied from 10 ml to 100 ml. Figure 8 shows the linear dependence of the volume of the aqueous solution on the limiting current, when it was less than 60 ml. But over this volume the plot became concave upward.

(B) Differential Pulse Polarography of Cadmium Oxinate

In addition to its applicability for dc polarography, differential pulse polarography turns out to be suited to the direct determination of a low concentration of metal ion after extraction.[13] In differential pulse polarography a linear dc ramp voltage is applied to the electrochemical cell and a fixed height pulse voltage is superimposed on the ramp voltage near the end of the life of each drop. The readout is the difference between two currents sampled immediately before and after the application of the pulse voltage.[14]

Polarogram of Cadmium Oxinate. Extractions were carried out by taking 80 m*l* of the aqueous phase and 80 m*l* of 0.1*M* oxine 1-butanol solution at 15±0.5°C. Figure 9 is the typical differential pulse polarogram of cadmium oxinate. The instrumental parameters are as follows; drop time 2 seconds, scan rate 0.5 mV/sec, pulse amplitude 50 mV, current range 1 μA. The dotted line is the residual current of a supporting electrolyte in 0.1*M* oxine 1-butanol. The peak potential of cadmium oxinate in 0.1*M* $LiClO_4$ solution is −0.62 volt versus aqueous SCE.

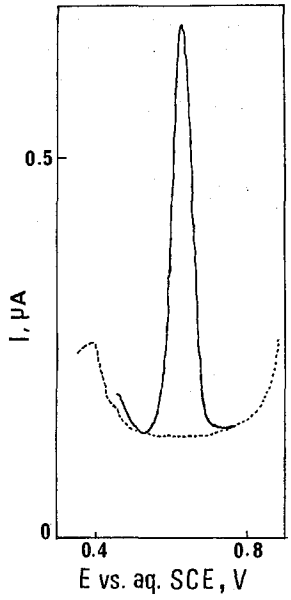

Fig. 9. Differential pulse polarogram of Cd(II)-oxinate. scan rate 0.5 mV/sec, modulation amplitude 50 mV, current range 1 μA, drop time 2 sec, pH 5.8–6.1, V_0/V_w 20/80 ml

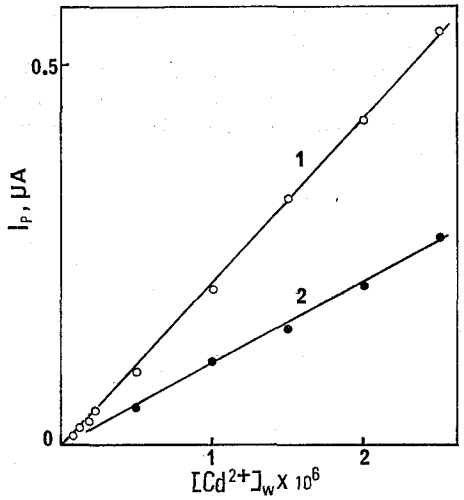

Fig. 10. Calibration curves of Cd(II) using differential pulse polarography.
1) after extraction,
2) aqueous solution

Calibration Curves of Cadmium. Solvent extractions were carried out by taking 80 m*l* of the aqueous phase containing different amounts of cadmium ion and 20 m*l* of 0.1*M* oxine 1-butanol solution. And in the case of the analysis of the organic phase after extraction and of the aqueous phase without extraction, polarograms were recorded in a concentration of 0.1*M* $LiClO_4$ as a base electrolyte. In Fig. 10 are plotted the linear calibration curves relating the peak current to the concentration under the constant instrumental parameters. The low peak currents in 1-butanol solution, compared to the aqueous solution, will be due to the higher value of viscosity coefficient in 1-butanol than that in water. Under the above given conditions the most concentrated point and the more dilute points seem to be deviations from the straight line in each case.

REFERENCES

(1) Z. P. Zagorski and M. Cyrankowska, "Advances in Polarography" vol. 2, p 584, I. S. Longmuir, ed., Pergamon, London, 1960.
(2) T. Fujinaga, H. Brodowsky, T. Nagai, and K. Yamashita, *Rev. Polarog.* (Kyoto), **11**, 217 (1963).
(3) B. K. Afghan and R. M. Dagnall, *Talanta*, **13**, 1097 (1966).
(4) T. Fujinaga and B. K. Puri, *Z. Anal. Chem.*, **269**, 340 (1974).
(5) T. Kitagawa and A. Ichimura, *Rev. Polarog.* (Kyoto), **19**, 25 (1973).
(6) For example, T. Fujinaga and K. Izutsu, *Int. Union Pure Appl. Chem.*, **27**, 275 (1971).
(7) G. Jones and S. M. Christian, *J. Amer. Chem., Soc.*, **61**, 82 (1939).
(8) R. G. W. Hollingshead, "Oxine and Its Derivatives", vol. I and II, p 191 (Bi), p 210 (Cd), p 227 (Co), p 237 (Cu), p 280 (Fe), p 316 (Pb), p 428 (Mo), Butterworths, London, 1954.
(9) J. A. Riddick and W. B. Bunger, "Techniques of Chemistry", 3rd ed., vol. II, "Organic Solvents", A. Weissberger ed., Wiley-Intersceince, New York, 1970, p 151.
(10) L. Meites, "Handbook of Analytical Chemistry", 3rd ed., McGraw-Hill, New York, 1963, 5–81.
(11) J. Stary, *Anal. Chim. Acta*, **28**, 132 (1963).
(12) H. A. Mottola and H. Freiser, *Talanta*, **13**, 55 (1966).
(13) J. H. Christie, J. Osteryoung, and R. A. Osteryoung, *Anal. Chem.*, **45**, 210 (1973).
(14) "Instructional Manual, Polarogrphic Analyzer, Model 174" V-19, Princeton Applied Research Corp., Princeton, 1971.