# Polarographic Determination of Bismuth, Copper, Iron(III), Palladium, and Uranium(VI) after Extraction into Molten Naphthalene with Oxine

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A rapid extraction-polarographic method has been developed for the direct determination of bismuth, copper, iron(III), palladium, and uranium(VI) extracted into the organic phase. Oxinates of metals were extracted into molten naphthalene at different pH values. With lowering of temperature, naphthalene separated out as a solid containing the metal oxinates. The solid mass was dissolved in DMF and the polarograms were recorded in the presence of a suitable supporting electrolyte. The metal oxinates give well defined waves. The relation between diffusion current and concentration is linear over a wide range of concentration with an average relative error not more than 1.05%. Interferences of various ions have been studied of the anions studied, only EDTA interfered in the extraction of bismuth, copper, iron(III), and uranium(VI). Of the cations studied, palladium interfered in the determination of bismuth, copper, iron(III), and uranium(VI). However, the intereference was eliminated by carrying out extraction first at low pH. In the determination of bismuth only copper interfered but its interference can also be eliminated as in the case of palladium. In the case of copper determination, only iron(III) interfered. In the determination of iron, copper interfered but interference can be eliminated by using a suitable masking agent. The determination of palladium and uranium(VI) is free from all interferences.

Of the heterocyclic nitrogen compounds, 8-quinolinol (oxine) reacts with more than fifty elements.1) Studies on the use of this reagent in solvent extraction revealed that even with proper control of pH, the reagent is not selective in extracting specific elements, although many masking agents have also been examined.2) The selectivity can be achieved by polarographic determination of metals after extracting into the organic phase. All the methods involve the use of mixed solvents, *i.e.* the extract is mixed with some other solvent in order to obtain well defined waves.3–5) There are two disadvantages: (a) the sensitivity is much decreased since the amount of organic solvent used for the extraction is large, (b) the pH of the extract has to be readjusted in order to match the conditions with the standard.

We have developed a new method in which the metal complex is extracted with molten naphthalene and separated from the aqueous phase by solidification and subsequent filteration or decantation. Since the extraction is carried out at high temperature, the equilibrium in the two phases is attained rapidly and the complexes are extracted merely by contact with molten naphthalene. The main advantage is that a very small amount of the organic phase is required for complete extraction in order to get well defined waves and better sensitivity. The method has been tested and found successful for the extraction and polarographic determination of cadmium,6) lead,6) molybdenum,7) indium,8) and nickel.9) In the present study, bismuth, copper, iron(III), palladium, and uranium(VI) have been extracted by this technique and determined polarographically. Elements such as Be(II), Hg(II), Sn(IV), Ti(IV), V(V), Cr(III), W(VI), Ce(IV), Co(II), Ga(III), Mn(II), Zn(II), and Zr(IV) can also be extracted by this technique, but they are not reduced at the dropping mercury electrode under these conditions, *i.e.* from 0.0 to $-1.1$ V. Above this potential oxine itself starts giving its own current. Interferences of various ions have been studied in detail. The method can be applied to the determination of these metals in complex materials.

## Experimental

*Reagents.* All the metal salts solutions were prepared from G. R. samples in double distilled water, metal contents being controlled by classical methods (10). 0.1 M solution of oxine was prepared in alcohol. 2 M solution of pyridine, sodium perchlorate and perchloric acid were prepared as according to indicated in Table 2. Naphthalene and *N,N*-dimethylformamide (DMF) were also of G.R. grade and tested polarographically before use. Ammonia and perchloric acid were used for controlling the pH of the solutions.

*Equipment.* Polarograms in all cases were recorded at 25±0.5 °C with a Yanagimoto polarograph P-8 with three electrode systems. An H-type cell with fine porosite sintered glass disk betw.een the two compartments was used. A saturated calomel electrode used as a reference electrode was connected to one compartment of the polarographic cell through potassium chloride agar-bridge. Dropping mercury electrode had the following characteristics, *m*: 1.52 mg/s, *t*: 4.78 s, and *H*: 60 cm in DMF with open circuit. In all instances the solution was deaerated with nitrogen for five minutes before recording the polarogram. A Hitachi pH-meter with glass electrode was used.

*Metal Oxinates Standard in DMF.* Aliquots of metal solutions were taken and precipitated with oxine,11) filtered, washed with cold water, dissolved in DMF, transferred to 100 ml measuring flasks and made exactly 100 ml with DMF in each case. The solutions were used for studying the polarographic behaviour of metal oxinates in DMF.

*General Procedure.* An aliquot of each metal solution was taken separately. To this was added 1.0 ml of the reagent (oxine), the pH being adjusted as given in Fig. 2 after being transferred to round bottomed flasks with stopper and heated in a water bath at about 60 °C, 2 g of naphthalene was added, heating in the water bath being continued till naphthalene melted and formed a separate liquid layer. This was stirred vigorously till the naphthalene separated out as a solid mass. Once again the contents were heated in the water bath to remelt the naphthalene, shaken vigorously and allowed to stand. Naphthalene was separated from the aqueous phase by filteration, dried in the folds of the filter paper and dissolved in warm DMF (*ca.* 40 °C).

Table 1. Effect of naphthalene on the polarograms of iron(III) and palladium oxinates

| Amount of naphthalene added, g | Amount of Fe(III) added: 168.00 μg<br>Perchloric acid: 0.1 M<br>Pyridine: 0.1 M | | | | Amount of Pd(II) added: 106.00 μg<br>Sodium perchlorate: 0.1 M<br>Pyridine: 0.1 M | | | |
|---|---|---|---|---|---|---|---|---|
| | Specific conductivity $\Omega^{-1}$ cm$^{-1}$ at 35 °C | Viscosity of the solution centipoise at 35 °C | $i_d$ for Fe(III) in mm | $E_{1/2}$ for Fe(III) in V | Specific conductivity $\Omega^{-1}$ cm$^{-1}$ at 35 °C | Viscosity of the solution centipoise at 35 °C | $i_d$ for Pd(II) in mm | $E_{1/2}$ for Pd(II) in V |
| 0.00 | $4.000\times10^{-3}$ | 1.164 | — | — | $4.545\times10^{-3}$ | 1.036 | — | — |
| 0.30 | $3.906\times10^{-3}$ | 1.205 | 76.00 | −0.10 | $4.166\times10^{-3}$ | 1.055 | 78.00 | −0.25 |
| 0.60 | $3.846\times10^{-3}$ | 1.210 | 76.00 | −0.10 | $4.000\times10^{-3}$ | 1.063 | 70.00 | −0.20 |
| 0.90 | $3.787\times10^{-3}$ | 1.218 | 76.00 | −0.10 | $3.937\times10^{-3}$ | 1.073 | 69.00 | −0.18 |
| 1.20 | $3.676\times10^{-3}$ | 1.234 | 76.00 | −0.12 | $3.846\times10^{-3}$ | 1.095 | 68.00 | −0.18 |
| 1.50 | $3.521\times10^{-3}$ | 1.247 | 75.00 | −0.12 | $3.703\times10^{-3}$ | 1.109 | 68.00 | −0.18 |
| 1.80 | $3.333\times10^{-3}$ | 1.284 | 72.00 | −0.12 | $3.597\times10^{-3}$ | 1.129 | 66.00 | −0.18 |
| 2.10 | $3.184\times10^{-3}$ | 1.320 | 68.00 | −0.12 | $3.448\times10^{-3}$ | 1.145 | 63.00 | −0.18 |

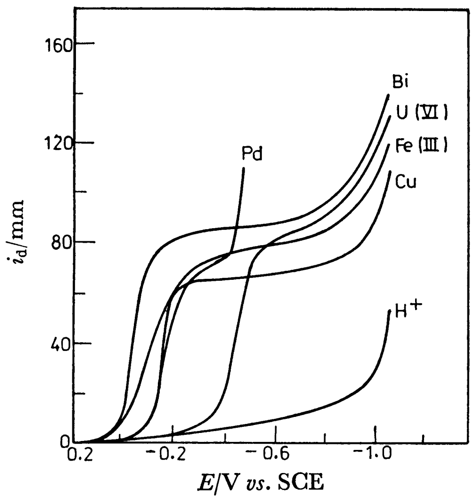

Fig. 1. Polarographic waves of metal oxinates in DMF. Bismuth: 82.80 μg, perchloric acid: 0.1 M, naphthalene: 1.0 g drope time: 4.78 s, $H$: 60 cm and the recorder sensitivity: $5\times10^{-9}$ A/mm. Copper: 79.37 μg, sodium perchlorate: 0.1 M, recorder sensitivity: $10\times10^{-9}$ A/mm, rest of the conditions are the same as for bismuth. Iron(III): 168.00 μg, pyridine: 0.1 M +0.1 M perchloric acid, recorder sensitivity: $7\times10^{-9}$ A/mm, rest of the conditions are the same as for bismuth. Palladium: 106.00 g, 0.1 M sodium perchlorate+0.1 M pyridine, recorder sensitivity: $3\times10^{-9}$ A/mm, rest of the conditions are the same as for bismuth. Uranium(VI): 95.21 μg, recorder sensitivtiy: $3\times10^{-9}$ A/mm, rest of the conditions are the same as for iron(III).

A supporting electrolyte of appropriate type was added in each case, the volume being made exactly 20 ml with DMF in a measuring flask. 10 ml of the solution was taken separately in the polarographic cell and deaerated with pure nitrogen for 5 min. The polarogram was recorded, in each case $i_d$ being referred to the calibration curve prepared under similar conditions.

Preliminary observations indicated that the metal oxinates give well defined waves (Fig. 1). Bismuth: 0.1 M perchloric acid (solution prepared in DMF), copper: 0.1 M $NaClO_4$ (solution of $NaClO_4$ in $H_2O$), iron and uranium: both in 0.1 M $HClO_4$ in DMF+0.1 M pyridine in $H_2O$ (waves were not diffusion controlled when both the electrolytes solutions were prepared in DMF) and palladium: 0.1 M pyridine+0.1 M $NaClO_4$ (both electrolytes in DMF, aqueous solutions of the electrolytes gave distorted waves for palladium). In the case of palladium two waves appeared in the supporting electrolytes. Only the first wave was used for the analysis since a large maximum appeared on the second wave which was not supressed with the use of common maxima supressors.

*Effect of Naphthalene on the Polarograms of Metal Oxinates.* Aliquots of the metal oxinates solutions were taken individually (Bi: 82.80 μg, Cu: 79.37 μg, Fe(III): 168.00 μg, Pd: 106.00 μg, and U(VI): 95.21 μg) in the polarographic cell. The amount of naphthalene was varied from 0.0—2.1 g by adding a different volume of its 30% solution in DMF. The supporting electrolytes were added, the final volume being made 10 ml with DMF. The solution was deaerated and the polarograms were recorded. In case of bismuth, copper and uranium(VI), $i_d$ remained constant up to 1.8 g of naphthalene added. Above this amount, $i_d$ started decreasing slightly due to the increase in the viscosity of the medium given in Table 1. The wave for iron(III) and palladium developed only in the presence of naphthalene, *i.e.* in the absence of naphthalene a large current appeared. The large current might be due to the streaming effect eliminated in the presence of naphthalene which increases the viscosity of the medium (Table 1). In case of iron(III), $i_d$ remained constant in the range 0.3—1.5 g of naphthalene and 0.6—1.5 g of palladium. In general, $E_{1/2}$ remained almost constant in all cases but $i_d$ started decreasing when the amount of naphthalene exceeded a certain amount, obviously due to the further increase in the viscosity of the medium.

*Effect of the Chelating Agent on the Polarograms of Metal Oxinates.* Aliquots of the metal oxinates solutions were taken under conditions similar to those described above. To these were added supporting electrolytes, 1 g of naphthalene in the form of 30% solution. The amount of oxine being varied from 0.0—75.0 mg by adding different volume of its 5% solution in DMF. In all the cases except palladium, $E_{1/2}$ shifted towards negative direction. This indicates that the metals form stable oxinate complexes in the presence of excess of oxine, while palladium oxinate might be decomposed under these conditions. $i_d$ remained constant in the range 0.0—11.5 mg for bismuth, 0.0—18.25 mg for copper, 0.0—15.0 mg for iron(III), 0.0—75.0 mg for palladium and uranium(VI). Above this concentration of the oxine added,

Table 2. Polarographic characteristics of metal oxinates in the presence of 1 g of naphthalene in DMF

| Metal | Supporting electrolyte | $E_{1/2}$/V from log plot | $I$ | Range of concentration in μg/20 ml | Value of slope from log plot in mV | Remarks | Average relative error % |
|---|---|---|---|---|---|---|---|
| Bismuth | 0.1 M $HClO_4$ in DMF | −0.05 | 2.399 | 10.35—248.40 | 65.0 | Irreversible | 0.95 |
| Copper | 0.1 M $NaClO_4$ in $H_2O$ | −0.14 | 3.858 | 3.96—198.40 | 38.0 | Slightly irreversible | 0.78 |
| Iron(III) | 0.1 M $HClO_4$ in DMF + 0.1 M Pyridine in $H_2O$ | −0.11 | 1.466 | 11.20—324.80 | 87.0 | Irreversible | 0.97 |
| Palladium | 0.1 M Pyridine + 0.1 M $NaClO_4$ both in DMF | −0.18 | 1.259 | 10.60—212.00 | 76.85 | Irreversible | 0.05 |
| Uranium(VI) | 0.1 M $HClO_4$ in DMF + 0.1 M Pyridine in $H_2O$ | −0.45 | 1.398 | 5.95—190.40 | 64.75 | Reversible | 0.88 |

Drop time: 4.78 s, $m$: 1.52 mg/s, $H$: 60 cm. Recorder sensitivity, bismuth: $5\times10^{-9}$ A/mm, copper: $10\times10^{-9}$ A/mm, iron(III): $7\times10^{-9}$ A/mm, palladium: $3\times10^{-9}$, and uranium(VI): $3\times10^{-9}$ A/mm.

the lower plateau in the case of bismuth and iron(III) became distorted. A prewave might start appearing in the presence of higher amount of oxine before the actual wave which was not fully developed. In the case of copper a maximum appeared in the higher amount of oxine added.

*Effect of Water on the Polarograms of Metal Oxinates*: Aliquots of each metal oxinate solution were taken separately in a polarographic cell. The amount of water was varied from 0.0—1.5 ml in different steps. The total volume of the solution was kept 10 ml in each case. In the case of bismuth 0.4 ml of water had no effect on $i_d$ on the shape of the polarogram but above this amount of water, $i_d$ started decreasing. A part of naphthalene might be separated in the colloidal state which would hinder the diffusion of the metal ions. The wave was drawn out at 1.5 ml of the water added. For this amount of water, naphthalene was separated out which increases the resistance of the medium, giving a drawn out wave for bismuth. 0.5 ml of water can be tolerated in case of copper, above this volume $i_d$ started decreasing but $E_{1/2}$ remained constant. In the case of iron(III), 0.7 ml of water can be tolerated but above this volume a maximum appearing might be due to the streaming effect. Only 0.2 ml of water can be tolerated in the case of palladium above this amount $i_d$ started decreasing though $E_{1/2}$ remained constant. The wave of palladium is very sensitive to water as indicated in the preliminary observations. In the case of uranium(VI), $i_d$ started decreasing and $E_{1/2}$ started shifting towards positive potential when the amount of water exceeded 0.4 ml. The uranium complex might be decomposed under these conditions.

The linear dependence of the limiting current on the square root of the height of mercury column indicates that the rate of reduction of these metal oxinates is diffusion controlled. The plot of log $i/i_d - i_d$ *vs.* $E$ gives a straight line. The values of slopes and $E_{1/2}$ calculated from the plot are given in Table 2. Copper undergoes reduction slightly irreversible with two electron change while uranium(VI) undergoes reduction reversibly with one electron change, bismuth, iron(III), and palladium are reduced irreversibly. The graph plotted between the concentrations of metal oxinates and diffusion currents give straight lines over a wide range of concentration. The diffusion current constants were calculated using the Ilkovic equation, $I=i_d/Cm^{2/3}t^{1/6}$ and are also given in Table 2. They are constant, indicating that the method is as sensitive as most of the polarographic method in the aqueous media. The average relative error did not exceed 1.05%.

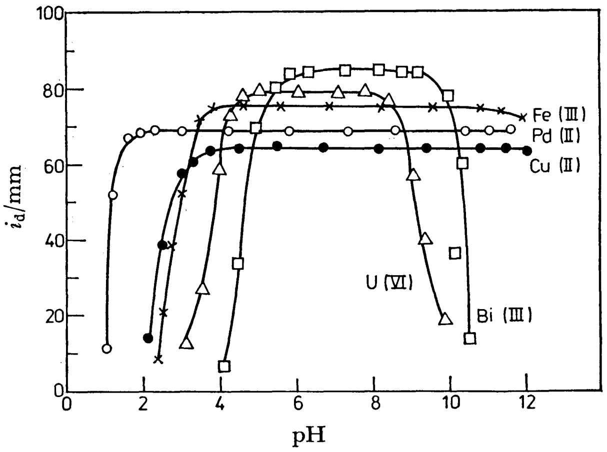

Fig. 2. Effect of pH on the extraction of bismuth, copper, iron(III), palladium, and uranium(VI). Naphthalene taken for each extraction: 2.0 g. Oxine used in each case: 1.0 ml of 1% solution in ethanol. Rest of the conditions are the same as Fig. 1.

*Effect of* pH *on the Extraction of Metals.* Extraction was carried out by the general procedure but at different pH. The effect is shown in Fig. 2.

*Effect of the Chelating Agent on the Extraction of Metals.* Extraction was carried out at different concentration of oxine. It was found that extraction was complete; Bi: 7—20 mg, Cu: 2.5—15.0 mg, Fe(III): 4.0—20 mg, Pd: and U(VI): 6.0—18 mg of the oxine added.

*Effect of Naphthalene on the Extraction of Metals.* Extraction was complete in all cases when the amount of naphthalene used was higher than 0.8 g, so 2.0 g was used for safe side.

*Effect of Aqueous Phase on the Extraction of Metals.* The volume of the aqueous phase was varied from 20 ml to 250 ml. The extraction was more than 99% when the volume of the aqueous phase did not exceed the following amounts:

Table 3. Effect of anions on the determination of bismuth, copper, iron(III), palladium, and uranium(VI)a)

| Salt added | Amount of ion added in mg | Bismuth found in μg | Copper found in μg | Iron found in μg | Palladium found in μg | Uranium found in μg | Remarks |
|---|---|---|---|---|---|---|---|
| Sodium citrate | 31.45 | 80.50 | 42.50 | 160.50 | 106.00 | 30.25 | Extraction completed |
| | 7.85 | — | 79.50 | 167.50 | — | 94.50 | at low concentration |
| Sodium oxalate | 33.60 | 80.75 | 65.20 | 122.50 | 105.50 | 35.50 | Same as above |
| | 3.36 | — | 80.50 | 166.66 | — | 94.00 | |
| Sodium borate | 20.20 | 81.25 | 79.50 | 168.00 | 106.00 | 95.50 | — |
| Sodium azide | 32.30 | 80.00 | 79.25 | 168.50 | 105.00 | 95.00 | — |
| Sodium fluoride | 22.60 | 81.00 | 75.25 | 167.75 | 105.50 | 35.40 | Extraction complete |
| | 11.30 | — | 79.50 | — | — | 94.00 | at low concentration |
| Sodium thiosulfate | 21.10 | 81.75 | 79.25 | 167.00 | 105.75 | 84.50 | — |
| Sodinm phosphate | 25.00 | 80.75 | 50.75 | 166.75 | 106.50 | 35.75 | Extraction complete |
| | 6.50 | — | 79.00 | 168.00 | — | 94.25 | at low concentration |
| Disodium EDTA | 40.00 | nil | nil | nil | 105.00 | 10.25 | No extraction in case of Cu, Bi, and Fe |
| Sodium potassium tartrate | 39.40 | 80.25 | 50.25 | 167.50 | 105.50 | 60.25 | Extraction complete |
| | 10.00 | — | 79.00 | — | 105.50 | 94.00 | at low concentration |
| Sodium sulfate | 40.00 | 80.00 | 79.50 | 168.50 | 106.00 | 95.25 | — |
| Potassum thiocyanate | 29.85 | 80.50 | 79.00 | 168.00 | 105.75 | 95.50 | — |
| Potassium chloride | 23.80 | 80.50 | 79.50 | 167.50 | 105.75 | 95.50 | — |
| Potassium bromide | 33.60 | 80.00 | 79.75 | 167.75 | 106.50 | 96.00 | — |
| Potassium iodide | 38.25 | 82.25 | 79.00 | 168.50 | 107.00 | 94.50 | — |

a) Conditions the same as those given in Fig. 2.

Table 4. Effect of cations on the determination of bismuth, copper, iron(III), palladium, and uranium(VI)a)

| Salt | Amount of foreign ion added in mg | Bismuth found in μg | Copper found in μg | Iron found in μg | Palladium found in μg | Uranium(VI) found in μg |
|---|---|---|---|---|---|---|
| Palladium chloride | 00.60 | 81.50b) | 80.75b) | 169.50b) | — | 95.00b) |
| Uranyl acetate | 00.56 | 80.50 | 80.00 | 168.25 | 106.50 | — |
| Tin(IV) chloride | 00.42 | 80.00 | 79.25 | 168.00 | 107.00 | 95.00 |
| Lead(II) nitrate | 0.66 | 81.00 | 79.50 | 169.00 | 106.25 | 95.75 |
| Sodium tungstate | 00.56 | 80.50 | 79.00 | 169.50 | 106.50 | 95.25 |
| Chromium(III) nitrate | 00.36 | 80.75 | 79.75 | 166.50 | 106.00 | 95.50 |
| Iron(III) chloride | 00.20 | 81.75 | c) | — | 107.00 | 95.50 |
| Copper(II) sulfate | 00.25 | 81.00b) | — | c) | 107.25 | 95.00 |
| Sodium vanadate | 00.43 | 80.75 | 79.75 | 168.00 | 106.50 | 95.25 |
| Bismuth nitrate | 00.43 | — | 79.50 | 168.75 | 106.75 | 95.00 |
| Thallium(I) nitrate | 00.76 | 80.50 | 79.00 | 168.25 | 106.00 | 95.50 |
| Mercury(II) chloride | 00.70 | 81.00 | 80.25 | 168.50 | 106.50 | 96.00 |
| Sodium molybdate | 00.39 | 80.25 | 79.00 | 167.50 | 105.00 | 94.50 |
| Nickel chloride | 00.25 | 81.00 | 78.50 | 167.50 | 106.75 | 96.00 |
| Cadmium chloride | 00.66 | 80.75 | 79.50 | 168.00 | 106.50 | 95.25 |
| Zinc nitrate | 00.22 | 79.75 | 80.00 | 169.00 | 106.00 | 95.25 |
| Manganese sulfate | 00.27 | 80.50 | 80.25 | 169.75 | 107.50 | 96.00 |

a) Conditions the same as those given in Fig. 2. b) Interfering cation removed by extraction at low pH. c) Determination not possible.

Bi: 120 ml, Cu: 100 ml, Fe(III): 105 ml, Pd: 190 ml, and U(VI): 150 ml. Extraction was not quantitative above the volume of the aqueous phase.

*Effect of Diverse Ions on the Determination of Metals.* The effect is given in Tables 3 and 4. Among the anions examined the extraction of bismuth, copper, iron(III), and uranium(VI) is not possible in the presence of EDTA. In the presence of citrate, oxalate, tartrate, phosphate, and fluoride, the results are low in the case of copper, iron(III), and uranium(VI). However, they are satisfactory in the presence of a relatively low concentrations of the anions. In the determination of bismuth, copper, iron(III), and uranium(VI), palladium interfered, but its interference can be eliminated by extracting palladium first at low pH and then the other metal ions were extracted from the aqueous phase at their proper pH values (Fig. 2). In the determination of bismuth only copper interfered but its interference can be eliminated as in the case of palladium. In the determination of copper, only iron(III) interfered while in the determination of iron(III), only copper interfered. The interference can be eliminated by using suitable masking agents.[12] There is no interference in the determination of palladium and uranium(VI).

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