The coloured solution are stable for two days, in properly seated tubes.

We are grateful to the CSIR, New Delhi, for the award of a junior research fellowship to one of us (N.S.R.).

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Solvent Extraction of Cu(II) Using 4-Isonitroso-3-methyl-1-phenyl-5-pyrazolone

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Received 9 *February* 1978; *accepted* 25 *May* 1978

Solvent extraction behaviour of Cu(II) using 4-isonitroso-3-methyl-1-phenyl-5-pyrazolone (HIMPP) in benzene as extracting agent has been studied. Composition of the extracted complex has been determined. Interference due to a number of foreign elements has also been tested.

IN an earlier investigation, Arora *et al.*[1] studied the solid metal complexes of 4-isonitroso-3-methyl-1-phenyl-5-pyrazolone (HIMPP). Presently we report the use of this ligand for the solvent extraction of Cu(II). Interferences due to most of foreign elements likely to be present in alloys, ores and industrial materials have been found to be negligible.

The ligand was prepared as described earlier[1] and its purity checked; m.p. 160°. It is soluble in benzene, alcohol and chloroform. Stock solution of copper (II) was prepared by dissolving known weight of pure metallic copper in dilute (1:1) nitric acid. The solution was evaporated to dryness and finally made up to a known volume with $0{\cdot}1N$ hydrochloric acid. Stock solution was diluted suitably to obtain Cu(II) solution containing copper equal to 10 μg per ml.

Procedure — An aliquot of $1{\cdot}6\times10^{-4}M$ copper solution (5 ml) and buffer solution (5 ml) were mixed and distilled water (10 ml) added to it. The mixture was shaken with a solution of HIMPP (20 ml) in benzene ($6{\cdot}16\times10^{-4}M$) for 5 min at $25° \pm 1°$. The two phases were allowed to separate. The amount of Cu(II) extracted into organic phase and that left unextracted into aqueous phase was determined spectrophotometrically using sodium diethyl dithiocarbamate reagent[2]. Copper present in the organic phase was stripped with 1:25 HCl (20 ml) prior to its determination. The distribution coefficients (D) were calculated as usual. In all the experiments the equilibrium *p*H was measured. In the same fashion experiments were conducted at constant *p*H 4·9 by varying the ligand concentration from 0·3 to 2 m*M*, keeping the copper concentration constant. It was observed that Cu(II) is almost completely extracted above *p*H 5·6 with $6{\cdot}16\times10^{-4}M$ HIMPP in benzene. The slope of the plots of log D vs *p*H and of log D vs log [HIMPP] is two in each case indicating that two moles of hydrogen ions are liberated in the extraction process and two moles of ligand are involved in complex formation. Hence the extraction process may be represented by the equation $Cu^{2+}+2HIMPP \rightleftharpoons Cu(IMPP)_2+2H^+$. The composition of the extracted complex is thus 1:2 (Cu-HIMPP).

In order to test the applicability of the method for the extraction of copper present in ores, alloys and industrial materials, etc. a number of interferences were examined by adding them to the aqueous solution containing 50 μg of Cu(II) and subjecting them to the general procedure maintaining the *p*H 5·4 and concentration of HIMPP $2{\cdot}46\times10^{-3}M$ in each case. In some cases tartaric acid was successfully used to prevent hydroxide formation. The results indicate that barring Al(III) and Sn(IV), none of the foreign cations added (1 mg each) hinders the complete extraction of Cu(II). The organic phase in each case was back washed with 1:25 HCl solution and analysed for Cu(II) and also for interfering elements, if any. It was observed that Ni(II), Be(II), Mg(II), Ca(II), Mn(II), Fe(III), Al(III), Th(IV), Sn(IV), Ti(IV), V(V) and U(VI) are not at all extracted alongwith Cu(II) whereas citrate, oxalate and ethylenediaminetetraacetate anions seriously interfere. Phosphate and sulphate anions at 100 mg level are without any effect on the extraction of Cu(II).

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o-Mercaptoacetamidobenzoic Acid as a Gravimetric Reagent for Zr(IV)

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Gravimetric determination of zirconium in pure salts as well as in zircon has been carried out using *o*-mercaptoacetamidobenzoic acid (*o*-MAB). The results obtained are comparable to those obtained with mandelic acid. The solid complex has been isolated and its IR data reported.

SEVERAL organic reagents have been tried[1-9] for the gravimetric determination of zirconium in its salts, alloys and ores. Since zirconium has a less tendency to form stable complexes with sulphur donor ligands it was of interest to see if *o*-mercaptoacetamidobenzoic acid (*o*-MAB), which has a —COOH group, besides —SH and —N donor sites, will form a complex with zirconium. It was found that zirconium forms a very stable complex with *o*-MAB and this can successfully be used for the quantitative determination of zirconium in the pH range 2·0-2·2. Zirconium was estimated as ZrO_2 after igniting the precipitate.

The reagent was prepared by the condensation of thioglycollic acid and anthranilic acid in the presence of a few drops of piperidine. The reagent was characterized by its IR spectrum and elemental analyses (Found: C, 51·2; H, 5·01; N, 7·1%. Reqd: C, 50·93; H, 4·75; N, 6·6%); m.p. 149°. Equivalent weight was found out to be 106·1.

o-MAB was used in the form of a 10% solution in 1:1 aqueous alcohol. 1 ml of this solution is sufficient for the determination of 0·0055 g of ZrO_2. Only a slight excess of the reagent should be used since *o*-MAB is not very soluble in water and may precipitate thus causing interference.

Zirconium can be accurately determined in the convenient range of 0·05-0·2 g. Zirconyl chloride solution was prepared in 0·1*N* hydrochloric acid and standardized using mandelic acid as the precipitating agent[4]. Precipitation with *o*-MAB was carried out as follows:

$ZrOCl_2$ solution (10 ml) was diluted to 150 ml. After adjusting the pH of the solution between 2·0 and 2·2 10% hot solution (20 ml) of the reagent in 1:1 aq. ethanol was added with constant stirring. The precipitate was digested for 30 min at 80-90° and cooled. It was filtered after 1 hr through Whatman filter paper No. 42, washed with a hot solution of the reagent, dried and ignited to constant weight in a platinum crucible and weighed as zirconium dioxide. The result obtained (0·1098 g) was in good agreement with the amount estimated with mandelic acid (0·1096 g).

The interference of the following ions when present to the extent of 25% of that of zirconium has been studied. Aluminium, nickel, calcium, iron, cerium ,uranyl, tin, lead, germanium and nitrate ions did not interfere (Table 1). Serious interference was observed only with thorium, titanium, vanadium and lanthanum. Similarly fluoride added as a sodium salt also caused interference. Tantalum, niobium and tungsten are not usually present in chloride solution. Other elements have not been investigated but they rarely occur in association with zirconium.

Well powdered zircon was converted to zirconium oxychloride[10] taking care to remove all interfering ions. A stock solution was then prepared and a suitable aliquot was estimated using *o*-MAB. The results thus obtained compared favourably with those given by mandelic acid method.

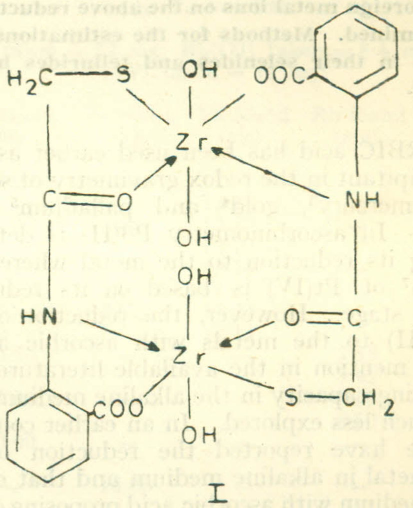
The yellow crystalline complex is soluble in acetone, benzene and ethanol. The analysis of the chelate displayed the metal ligand ratio to be 1:1 (Found: ZrO_2, 37·5; C, 33·1; H, 3·4; N, 4·5; S, 10·1%. Requires ZrO_2, 36·8; C, 32·31; H, 2·89; N, 4·18; S, 9·6%). The infrared spectra of the zirconium chelate indicated the absence of the characteristic absorptions for —SH and —COOH groups. However, the strong absorption of the ligand at 1670 and 3360 cm⁻¹ due to $\nu C{=}O$ and νNH are shifted to lower frequencies in the chelate and appear at 1630 and 3340 cm⁻¹ respectively. These shifts towards lower frequency show that NH and Co are involved in coordination. The absence of a band around 1100-800 cm⁻¹ due to $\nu Zr = O$[11-14] rule out the possibility of Zr=O bond in the chelate.

TABLE 1 — EFFECT OF DIVERSE IONS ON THE GRAVIMETRIC ESTIMATION

[Amount of diverse ion, ~25% of ZrO_2 taken of Zr(IV)]

Ion	ZrO_2 taken g	ZrO_2 found g	Difference g
Ni^{2+}	0·1098	0·1096	− ·0002
Ca^{2+}	0·1098	0·1096	− ·0002
Fe^{3+}	0·1098	0·1100*	+ ·0002
Al^{3+}	0·1098	0·1094	− ·0004
La^{3+}	0·1098	0·1012	− ·0086
Th^{4+}	0·1098	0·1184	+ ·0086
Ce^{4+}	0·1098	0·1094*	− ·0004
UO_2^{2+}	0·1098	0·1094*	− ·0004
Ti^{4+}	0·1098	0·1296	+ ·0914
Sn^{2+}	0·1126	0·1124	− ·0002
Pb^{2+}	0·1126	0·1124	− ·0002
V^{5+}	0·1126	0·1208	+ ·0082
Ge^{4+}	0·1126	0·1130*	+ ·0004
NO_3^-	0·1098	0·1094	− ·0004
SO_4^{2-}	0·1098	0·1094	− ·0004
F^-	0·1098	0·1058	− ·0040

*Double precipitation.



I

On steric grounds, one can assign a dimeric structure (I) for the complex. The dimeric structure involves less strain than the monomeric structure. Molecular weight of the complex in benzene was found out by ebullioscopy to be 670±15. This provides additional support to the dimeric structure.

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Reduction of Pd(II), Rh(III) & Pt(IV) by Ascorbic Acid in Strongly Alkaline Medium—Gravimetric Determinations in Their Selenides & Tellurides

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Received 27 *April* 1977; *revised* 1 *May* 1978; *accepted* 25 *May* 1978

Quantitative reduction of Pd(II), Rh(III) and Pt(IV) to the respective metals by ascorbic acid in strongly alkaline medium has been studied. Three to 30 mg of palladium, 4·2 to 25·2 mg of rhodium and 4 to 24 mg of platinum have been determined gravimetrically with accurate and reproducible results. The interferences of various foreign metal ions on the above reductions have been examined. Methods for the estimations of these elements in their selenides and tellurides have been proposed.

ASCORBIC acid has been used earlier as a metal precipitant in the redox gravimetry of selenium[1], silver[2], mercury[3], gold[4] and palladium[5] in acid medium. In ascorbinometry Pd(II) is determined[6] following its reduction to the metal whereas determination[7] of Pt(IV) is based on its reduction to divalent stage. However, the reduction of Pt(IV) or Rh(III) to the metals with ascorbic acid does not find mention in the available literature, further its reducing capacity in the alkaline medium appears to be much less explored. In an earlier communication[8] we have reported the reduction of Cu(II) to the metal in alkaline medium and that of Te(IV) in acid medium with ascorbic acid proposing a method for the analysis of copper tellurides. Reduction of Ag(I) and Au(III) with ascrobic acid in strongly alkaline medium were made the basis for their determinations in their selenides and tellurides in our recent paper[9].

The data recorded in this note pertain to the reductions of Pd(II), Rh(III) and Pt(IV) to the metals is strongly alkaline medium. Methods for the determinations of Pd(II), Rh(III) and Pt(IV) in their selenides and tellurides have been suggested.

It was observed that the reduction of Pt(IV) alone with ascorbic acid in alkaline medium was slow and incomplete. However, it was found that, metal ions which undergo fast reduction with ascorbic acid, induce the reduction of Pt(IV). Ag(I) is used for this purpose throughout the study. A few results of Pt(IV) reduction induced with Au(III) and Cu(II) are also recorded in Table 1.

The reduction of Pd(II), Rh(III) and induced reduction of Pt(IV) were quantitative between 1 to 5M NaOH medium. However, the reduction of Pd(II) became slower with increase in NaOH molarity from 1 to 5. Determinations of the metal ions in pure solutions were therefore carried out in 1M NaOH medium for convenience while during their estimations in selenides and tellurides, the NaOH molarities were maintained at 2-3M in order to keep Se(IV) and Te(IV) completely in solution.

Stoichiometric amounts of ascorbic acid were found to be adequate for all the three reductions, however, excess reagent was used in the subsequent determinations. Reduction of Rh(III) does not take place in cold whereas Pd(II), contrary to its behaviour in acid medium[5], and Pt(IV) could be reduced at room temperature quantitatively within 30 min. Some results pertaining to these experiments are recorded in Table 1. Minimum quantity of Ag(I) necessary for the quantitative reduction of Pt(IV) was one-fourth that of Pt(IV) taken.

The statistical evaluation of the results shows that the maximum errors are 1·66, 2·38 and 1·25% for palladium, rhodium and platinum respectively. However, the above figures mostly pertain to the lowest concentration range studied.

The method proposed for tellurides and selenides possesses a special feature that after determination of palladium, rhodium or platinum in alkaline medium selenium or tellurium could be reduced and estimated in the filtrate with the same reagent by simply rendering the medium acidic. However, the determinations of selenium and tellurium are not included in the present work since their reductions in acid medium are already established[1,8].

Pd(II), Rh(III) and Pt(IV) chloride solutions were prepared by dissolving the corresponding chloride (Johnson Matthey or Arora Matthey, 1 g) in a minimum amount of 1:1 HCl, made up to 500 ml and standardized complexometrically[10] in case of Pd(II) and gravimetrically with thionalide [Rh(III)] and formic acid [Pt(IV)]. One ml of the each solution contained 1·2 mg of Pd(II), 0·84 mg of Rh(III) and 0·80 mg of Pt(IV).

Silver(I) nitrate solution was prepared by dissolving 1 g high purity silver in minimum amount of HNO_3 1·2 sp.gr. and made up to 1 litre. Selenium(IV) solution was prepared by dissolving 0·702 g selenium dioxide (Johnson Matthey) in 50 ml of conc. HCl, diluted to 500 ml and standardized. Tellurium(IV) solution was prepared by dissolving 0·50 g of tellurium metal by boiling with conc. HCl (50 ml), made up to 500 ml and standardized. Sodium hydroxide solution (10M) was prepared from BDH(AR) reagent and stored in polythene bottle. Solutions of various metal ions having concentration of 1 mg/ml were prepared from respective AR salts. Ascorbic acid GR (S. Merck) was used as solid. All other chemicals used were of analytical reagent grade.

Determination of palladium and rhodium in their pure solutions — An aliquot of Pd(II) solution containing 3 to 30 mg of Pd(II) or Rh(III) solution corresponding to 4·2 to 25·2 mg Rh(III) was taken and to this was added 10M NaOH (10 ml) and diluted to 100 ml. Crystalline ascorbic acid (0·2 g) was introduced and the solution boiled for 5 to 10 min to coagulate the precipitated metal. In the case of palladium the metal was filtered through

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