# Spectrophotometric Determination of Zirconium with 5,7-Diiodo-8-hydroxyquinoline

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5,7-Diiodo-8-hydroxyquinoline (diiodo-oxine) has been used as an analytical reagent for the spectrophotometric determination of zirconium with which it forms a yellow colored complex (1 : 2) in dilute hydrochloric acid solution. The complex is extractable into chloroform from 0.1—0.2 mol $dm^{-3}$ HCl showing an absorption maximum at 417.5—421 nm with a molar absorptivity of $1.87\times10^4$ $dm^3\,mol^{-1}\,cm^{-1}$ and Sandell sensitivity equal to $4.8\times10^{-3}$ μgZr $cm^{-2}$. Beer's law holds good in the range 0—5 μgZr $cm^{-3}$, with a standard deviation ±0.006 and relative mean error ±0.36%. The method is simple, selective and sensitive.

Recent literature survey reveals that 8-hydroxyquinoline[1] (oxine) and its other derivatives namely, 7-iodo-8-hydroxyquinoline-5-sulfonic acid[2] (ferron) and 5,7-dibromo-8-hydroxyquinoline[3] (dibromo-oxine) have earlier been employed for the spectrophotometric determination of zirconium in acidic medium. During the course of investigations, it was thought that diiodo-oxine, which is another derivative of oxine, may possess identical chelating properties and with that end in view, it was considered worth to study its complexation behavior towards zirconium and the extraction possibilities with different organic solvents. This fact, on examination, forms the basis of the present method worked out for zirconium determination using solvent extraction technique with the following details:

## Experimental

**Apparatus and reagents:** UV-visible (Shimadzu-140-02) and U-2000 (Hitachi) spectrophotometers with 10 mm matched cells are used for absorbance measurements and other spectral studies, respectively.

A stock solution of zirconium is prepared by dissolving an accurately weighed amount of $ZrOCl_2\cdot8H_2O$ in 2.0 mol $dm^{-3}$ HCl to give 1 mgZr $cm^{-3}$. Aliquots are suitably diluted to give solutions at μgZr $cm^{-3}$ level. The solutions of other metal ions are prepared by dissolving their commonly available chemically pure salts in water or dilute hydrochloric or sulfuric acid to give $\leqslant$10 mg $cm^{-3}$ concentration of the ions.

5,7-Diiodo-8-hydroxyquinoline (diiodo-oxine) (Aldrich) is dissolved in acetone to give 0.1% (w/v) solution. Chloroform (Qualigens, SQ) is distilled and the fraction distilling between 60—61 °C is collected for use.

**Samples:** Synthetic samples are prepared by mixing zirconium and other metal ion solutions to get the desired composition.

**Procedure:** To an aliquot containing upto 50 μg Zr in a 50 $cm^3$ beaker, add 1.0 $cm^3$ of 0.1% diiodo-oxine reagent and 1.5 $cm^3$ of 1 mol $dm^{-3}$ HCl solution. Allow the contents to stand undisturbed for 10 min and then add enough distilled water to make the aqueous volume 10 $cm^3$. Heat up to 60 °C and allow it to cool. Transfer the contents carefully to a 100 $cm^3$ separatory funnel. It is then equilibrated once with 10 $cm^3$ of chloroform for 30 s taking care to release the pressure occasionally through the stop cock. After phase separation, the organic extract is passed through Whatman No. 41 filter paper (pretreated with chloroform) to remove water droplets. The absorbance of the yellow complex is measured at 420 nm against pure solvent using 10 mm cells.

In case of samples containing Fe, Cr, Ce, Sn, and Nb, the optimum amounts of masking agents required to be added to the aqueous solution prior to the addition of diiodo-oxine are: 10 mg ascorbic acid for each of Fe(III) 5 mg and Cr(VI) 0.2 mg, 100 mg thiourea for Ce(IV) 1 mg; tartrate 2 mg for Sn(II) 10 μg; and citrate 2 mg for Nb(V) 20 μg, in a final 10 $cm^3$ volume.

Finally, zirconium content in various samples is computed from the calibration curve prepared under optimum conditions of the procedure.

## Results and Discussion

Zirconium(IV) reacts with diiodo-oxine forming a light yellow colored species in neutral medium which gets intensified in acidic medium. The spectral characteristics, effect of variables and diverse ions on the absorbance of Zr(IV)–diiodo-oxine complex, stoichiometry and applications of the system are discussed below.

**Spectral Characteristics, Beer's Law and Sensitivity:** The absorption spectrum of the colored Zr(IV)–diiodo-oxine complex against reagent blank in chloroform under optimum conditions shows maximum at 417.5—421 nm (Fig. 1, Curve A). The spectrum of reagent blank against pure solvent '$CHCl_3$' shows that the reagent practically does not absorb above 400 nm

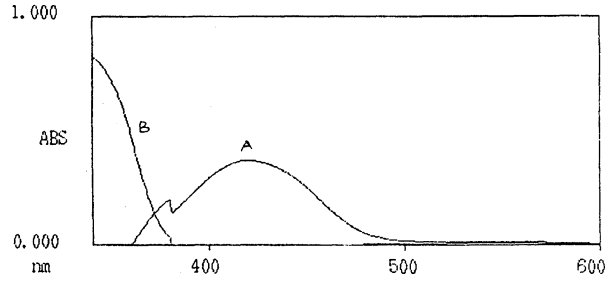


Fig. 1. Absorption spectrum of Zr(IV)–diiodo-oxine complex in chloroform. A: 1.9 μgZr cm$^{-3}$ measured against reagent blank. B: reagent blank measured against chloroform.

(Fig. 1, Curve B). Therefore, all the measurements are carried out at 420 nm against chloroform. The absorbance of the metal complex in chloroform shows linear response upto 5 μg cm$^{-3}$ of Zr and obeys Beer's law with a molar absorptivity of $1.87\times10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$. The optimum concentration range to measure zirconium accurately, as obtained from Ringbom's[4] plot (Fig. 2) at 420 nm, is 1.09—3.98 ppm. Sandell sensitivity of the method is $4.8\times10^{-3}$ μgZr cm$^{-2}$. Ten replicate determinations containing 2 μgZr cm$^{-3}$ give mean absorbance value of 0.41 with a standard deviation of ±0.006 and a relative mean error of ±0.36%.

**Effect of Different Parameters:** The effect of different variables like acidity, temperature, diiodo-oxine concentration, equilibration time, and color development time on the extraction of zirconium has been studied. In the study of these parameters, 10 cm$^3$ aqueous solution containing 2 μgZr cm$^{-3}$ is subjected to single extraction with an equal volume of benzene and the optimum value found for different parameters being kept

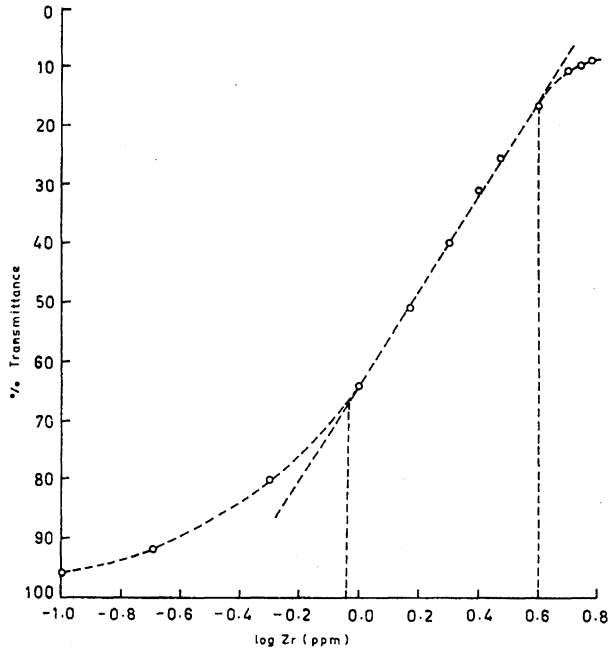


Fig. 2. Ringbom plot for Zr(IV)–diiodo-oxine complex.

constant except the one under study.

**Effect of Acidity:** Effect of acidity is examined in terms of absorbance of the complex in the organic phase. Maximum absorbance is obtained when extractions are carried out from 0.1—0.2 mol dm$^{-3}$ HCl, $CH_3COOH$ and $HClO_4$; but the absorbance remains constant only when HCl is used and therefore, hydrochloric acid medium is preferred for further investigations. The aqueous phase after extraction, when tested by arsenazo III method[5] is void of zirconium. Thus quantitative extraction of zirconium occurs in the entire acidity range. Phosphoric and sulfuric acids are also tried but not found suitable as the absorbances are quite low in these cases.

**Effect of Temperature:** The absorbance of the metal complex increases with the increasing temperature and attains constancy in the range 55—65 °C. If the temperature exceeds 65 °C, low results are obtained.

**Effect of Reagent Concentration:** While studying the influence of reagent concentration, it has been found that 0.5—2.0 cm$^3$ of diiodo-oxine (0.1% w/v in acetone) is sufficient to extract upto 50 μg of zirconium in a single contact. Higher reagent concentrations give low results and therefore, extractions are carried out using 1.0 cm$^3$ of the reagent each time.

**Effect of Equilibration Time:** After complexation under optimum conditions, the extraction of Zr(IV)–diiodo-oxine complex into the solvent is quick and no change is observed in the absorbance when shaking time is varied from 5—60 s. Hence, equilibration time of 30 s is considered sufficient.

**Effect of Color Development Time:** The formation of the complex between Zr(IV) and diiodo-oxine is slow and takes time to develop fully. If the color development time is kept 30 s, the absorbance of the complex is only 0.35 and increases to 0.375 for 5 min time. It is maximum at 0.39 when the reaction mixture (zirconium solution+reagent+acid) is allowed to stand undisturbed for 8—20 min. Thus it is desirable to keep 10 min as color development time for the complex.

**Choice of Extractant:** The complex is quantitatively extracted in a single contact with an equal volume (10 cm$^3$) of chloroform. Maximum molar absorptivity of the complex is observed with chloroform and hence it is preferred as extractant for the system. Aqueous phase after extraction is free from zirconium as indicated by testing the trace of metal ion, if any, with arsenazo III method.[5] With other solvents, the color intensity of the complex decreases in the order: benzene, carbon tetrachloride, toluene, dichloro ethane=ethyl methyl ketone, butanol, isobutyl methyl ketone=amyl alcohol, ethyl acetate, butyl acetate=amyl acetate, and cyclohexane. The $\lambda_{max}$ is independent of the nature of the solvent used. The absorbance of the complex remains practically constant for 2 h in chloroform.

From the consideration of the data obtained from the above mentioned parameters, optimum conditions for

the system are laid down as already described in the procedure.

**Effect of Diverse Ions:** The tolerance limits for many anions and complexing agents have been worked out (Table 1). It is found that ⩽100 mg each of nitrate, sulfate, acetate, thiourea and sulfosalicylic acid; ⩽50 mg of chloride; ⩽10 mg each of ascorbic acid, iodide, carbonate, hydroxylamine hydrochloride; ⩽5 mg of sulfite, and ⩽2 mg each of citrate and tartrate; added initially to the aqueous phase (10 $cm^3$) do not affect the absorbance of Zr(IV)–diiodo-oxine complex. Phosphate, fluoride, disodium dihydrogen ethylenediaminetetraacetate, hydrogen peroxide, oxalate, and thiocyanate interfere even in small amounts.

Under the optimum conditions of the procedure, the tolerance level of different metal ions is studied by carrying out determination of 20 μg zirconium in presence of each of the ions (Table 2) added to the aqueous phase (10 $cm^3$) before the addition of diiodo-oxine. Interference of Iron(III) and Chromium(VI) is eliminated by adding ascorbic acid which reduces them to Fe(II) and Cr(III), and are thus not extracted; whereas Ce(IV), Nb(V), and Sn(II) form non-extractable complexes with

Table 1. Effect of Anions and Complexing Agents on Zr(IV)–Diiodo-oxine Complex

| Salt added | Amount mg/10 $cm^3$ | Absorbance |
|---|---|---|
| None | — | 0.410 |
| Sodium nitrate | 100.00 | 0.410 |
| Sodium sulfate | 100.00 | 0.410 |
| Sodium acetate | 100.00 | 0.410 |
| Thiourea | 100.00 | 0.410 |
| Sulfosalicylic acid | 100.00 | 0.410 |
| Sodium chloride | 50.00 | 0.410 |
| Ascorbic acid | 10.00 | 0.410 |
| Potassium iodide | 10.00 | 0.410 |
| Sodium carbonate | 10.00 | 0.410 |
| Hydroxylamine hydrochloride | 10.00 | 0.410 |
| Sodium sulfite | 5.00 | 0.410 |
| Sodium citrate | 2.00 | 0.410 |
| Sodium potassium tartrate | 2.00 | 0.410 |
| Sodium phosphate | 10.00 | 0.016 |
| Sodium fluoride | 10.00 | 0.016 |
| Disodium dihydrogen ethylene diaminetetraacetate | 10.00 | 0.013 |
| Hydrogen peroxide[a)] | 1.00 | 0.012 |
| Sodium oxalate | 1.00 | 0.010 |
| Potassium thiocyanate | 1.00 | 0.004 |

Conditions: Zr=20 μg; diiodo-oxine=1.0 $cm^3$, HCl=1.5 $cm^3$ of 1.0 mol $dm^{-3}$; temperature=60°C; color development time=10 min; aqueous volume=solvent volume=10 $cm^3$; solvent=chloroform; equilibration time=30 s; no. of extractions=1. a) 6.0% added in $cm^3$.

Table 2. Effect of Different Cations on Zr(IV)–Diiodo-oxine Complex

| Metal ion | Amount mg/10 $cm^3$ | Absorbance |
|---|---|---|
| None | — | 0.410 |
| Ca(II),Ba(II),Hg(II), Th(IV),Sr(II),Zn(II), Pb(II),Bi(III),Mg(II) | 10.0 | 0.410 |
| Mn(II) | 8.0 | 0.410 |
| Al(III),Co(II),Ni(II), Cd(II),Fe(III)[a)] | 5.0 | 0.410 |
| U(VI) | 4.0 | 0.410 |
| Sb(III) | 2.5 | 0.410 |
| Se(IV) | 2.0 | 0.410 |
| Re(VII),Fe(II),Ce(IV)[b)] | 1.0 | 0.410 |
| Au(III) | 0.536 | 0.410 |
| Be(II) | 0.5 | 0.410 |
| Cu(II),Cr(VI)[a)] | 0.2 | 0.410 |
| Os(VIII) | 0.1 | 0.410 |
| Pt(IV) | 0.0975 | 0.410 |
| Ti(IV),Ir(III),As(III) | 0.05 | 0.410 |
| Ru(III),Nb(V)[c)] | 0.02 | 0.410 |
| W(VI),Sn(II)[d)] | 0.01 | 0.410 |
| Mo(VI) | 0.004 | 0.410 |
| Ta(V) | 0.05 | 0.360 |
| V(V) | 0.02 | 0.640 |

a) In presence of 10 mg ascorbic acid. b) In presence of 100 mg thiourea. c) In presence of 2 mg sodium citrate. d) In presence of 2 mg sodium potassium tartrate.

Table 3. Analysis of Samples by the Proposed Method

| S.No. | Sample composition | | Zr found[d)] |
|---|---|---|---|
| | Matrix[a)] | Zr added/μg | μg |
| 1. | Re (0.5), Be (0.2), Co (0.5), Mn (2), Cu (0.05) | 30 | 29.85 |
| 2. | [Fe (5)][b)] | 20 | 20.00 |
| 3. | Ba (2), Ca (2), Sr (2) | 16 | 15.68 |
| 4. | [Bi (0.5), Pb (0.5), Cd (2), Cr (0.02)][b)] | 15 | 14.75 |
| 5. | [Hg (2), Se (0.5), Ni (0.5), Nb (0.01)][c)] | 10 | 10.00 |
| 6. | Zn (4), Mg (4.5), Al (0.5), Pt (0.05) Ir (0.02), Os (0.05) | 10 | 10.05 |

a) Figure in brackets indicates the amount of the metal ions in mg. b) In presence of ascorbic acid. c) In presence of citrate. d) Average of triplicate results.

Table 4. Comparison of Proposed Method of Zirconium Determination with Some of the Existing Ones

| Reagent | Extraction solvent | pH or $[H^+]$ for extraction | $\lambda_{max}$ (nm) | Sandell sensitivity (or S) | Precision (rel. std. dev.) | Interferences (without masking agents) | Comments |
|---|---|---|---|---|---|---|---|
| 8-Hydroxyquinoline | $CHCl_3$ | 8.9 (w.r.t. $NH_3$–$NH_4Cl$ buffer) | 385 | 0.0064 | — | Nb,Ti,Al | No extensive study of interferences made |
| 5,7-Dibromo-8-hydroxyquinoline | $CCl_4$ | 1—2 M HCl | 340 | 0.006 | — | Mo(VI),V(V), Ti(IV),Cu(II) | — |
| 7-Iodo-8-hydroxyquinoline-5-sulfonic acid | TBA–$CHCl_3$ | 0.08—0.1 equiv $H_2SO_4$ | 400—405 | 0.006 | — | Cr(VI),Mo(VI), W(VI),V(V), Ti(IV),Fe(III), Cu(II),Sn(II), $PO_4^{3-}$,$F^-$,$C_2O_4^{2-}$, EDTA,citrate, tartrate | — |
| Quercetin | — | 0.1—1 M HCl | 440 | 0.004 | — | Sc,Ga,Hg(l),Ti, Hf,Th,Ge,Sn,V, Cr,Mo,W,Fe,Sb, Nb,Ta,Platinum Metals, $C_2O_4^{2-}$,$F^-$,$PO_4^{3-}$ | Separation required before analysis |
| Alizarin red S | — | 0.1—1.0 M $HClO_4$ | 520 | 0.013 | — | U(VI),Fe(III), $F^-$,$PO_4^{3-}$ | — |
| Pyrocatechol violet | — | 4.9—5.7 | 650 | 0.0028 | 2.0% | $La^{3+}$,$Ce^{3+}$, $Th^{4+}$,Al,Ti, V(IV),U(IV), Mo(VI),Fe(III,II), Citrate,oxalate, tartrate,$F^-$, EDTA | — |
| 4-(2-Pyridylazo)resorcinol | — | 2.4—2.6 | 540 | 0.013 | 1.3% | $CN^-$,$F^-$,EDTA, tartrate,citrate, Co(II),Ni,Cu, U(VI),Fe(II,III), Cd(II),Bi(III), Ce(IV) | — |
| 5,7-Diiodo-8-hydroxyquinoline | $CHCl_3$ | 0.1—0.2 M HCl | 417.5—421 | 0.0048 | — | V(V),Ta(V),$F^-$, $PO_4^{3-}$,$SCN^-$,$C_2O_4^{2-}$, EDTA (PROPOSED METHOD). | — |

thiourea, citrate, and tartrate, respectively. Tantalum(V) forms white precipitates with the reagent which stay back in the aqueous phase even on extraction and lowers the results; whereas V(V) gives greenish yellow color and interferes increasing absorbance values.

**Applications:** The wide applicability of the method is tested by the satisfactory analysis of a variety of synthetic samples containing zirconium upto 30 μg in the aliquot (Table 3). This method is quite selective for zirconium determination in the presence of large number of elements especially iron, chromium, uranium, cerium, rhenium, osmium, iridium, thorium, aluminium, magnesium, manganese, cobalt, copper, nickel, zinc, mercury, lead, bismuth, cadmium, beryllium, platinum, ruthenium, gold, arsenic, titanium, and niobium which seriously interfere in most of the existing methods of zirconium determination.[6] The proposed method compares well with the existing ones (Table 4) and offers the advantages of better sensitivity, selectivity, wider Beer's law range, applicability to samples containing several interfering elements in concentrations higher than normally met with and is simple, rapid, precise, and accurate.

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