

## The Analytical use of Tetrahydroxy-p-benzo-quinone for the Determination and Estimation of Cations

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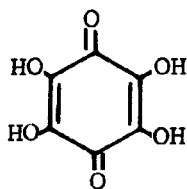
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**Summary:** Tetrahydroxy-p-benzoquinone (I) has been reported to react with large number of metal ions and has been used in estimations as metal indicator or precipitant. However, due to its non-selective nature and various colour reactions over a wide range of pH, the use of (I) in analytical separation has not been investigated in past. The work reported here has been carried out to explore the possibility of use of (I) in quantitative analysis of metals by gravimetric, spectrophotometric, titrimetric and atomic absorption methods. The experimental findings have also been employed in analysis of synthetic mixtures of cations so as to establish correlation of reactions between metals and reagent (I).

### Introduction

In analytical separations, coordination of organic reagents with metal ions to form complexes, chelates or polynuclear species have played an important role to detect and estimate cations or anions<sup>2,3,4,5</sup> quantitatively.

Most of the organic reagents used in complexation process possess one or more pairs of electrons available for sharing or complete transfer to electron deficient metal ions. Such lone pairs of electrons are characteristic of oxygen, sulphur, nitrogen and many other hetero elements present in straight chain or cyclic structure or functional groups of organic reagents.



( I )

The use of tetrahydroxy-p-benzoquinone (I) of its disodium salt in analytical separation of mixtures of cations and anions has been previously reported<sup>6,7</sup>. It has also been employed as metal indicator. However, no systematic study has been made to find its possible usages as selective, sensitive or specific organic reagent although it has four hydroxy groups at ortho position

available for chelation or complexation alongwith two-oxo-groups in benzoid structure which give it added importance as colour sensitive reagent. The (I) with various metals has remained obscure and analysts in the past have been interested only to use it to estimate and separate few cations such as lead structure, bismuth and to monitor titration end point.

### Experimental

#### *Preparation of series of Buffer Solutions.*

The buffer solutions were prepared using standard<sup>25,26</sup> procedures for maintaining pH of reaction mixture from 1 to 10.0, 0.1M. Aqueous solution of tetrahydroxy-p-benzoquinone was prepared by dissolving 1.72g of the reagent in water and diluting to 100ml. Similar procedure was adopted to prepare 0.01M solutions of various cations by dissolving appropriate salt or oxide into acid and diluting to 250ml.

2ml of buffer of different pH were placed in each test-tube separately in which 1.0ml of cations and 1.0ml of the reagent solution were also added. The contents of the test-tubes were thoroughly mixed and any further dilution of test solution was avoided so as to prevent drastic change in pH value or solubilization of the precipitates. Also the content of the test tubes were slightly warmed to facilitate mixing and dissolution of undesired salt or reactants.

Table 1. Metal tetrahydroxy-p-benzoquinones precipitation reactions using different concentrations.

S.No.	Metal Ion	Set	Total volume used.	g. moles of metal	g. moles of reagent	pH at which ppt. appears	colour of precipitate
1.	Lead	a	6.0 ml	$1.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	1-10	Purple
		b	5.0 ml	$2.0 \times 10^{-5}$	$1.0 \times 10^{-5}$	1-10	Purple
		c	5.0 ml	$2.0 \times 10^{-6}$	$1.0 \times 10^{-6}$	1-10	Purple
		d	6.0 ml	$1.0 \times 10^{-6}$	$3.0 \times 10^{-6}$	no ppt	Purple
		e	5.0 ml	$2.0 \times 10^{-7}$	$1.0 \times 10^{-7}$	no ppt	Purple
2.	Bismuth	a	6.0 ml	$1.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	1	Purple
		b	5.0 ml	$2.0 \times 10^{-5}$	$1.0 \times 10^{-5}$	1	Purple
		c	5.0 ml	$2.0 \times 10^{-6}$	$1.0 \times 10^{-6}$	1	Purple
		d	6.0 ml	$1.0 \times 10^{-6}$	$3.0 \times 10^{-6}$	1	Purple
3.	Lanthanium	a	6.0 ml	$1.0 \times 10^{-6}$	$3.0 \times 10^{-5}$	2-10	Purple
		b	5.0 ml	$2.0 \times 10^{-5}$	$1.0 \times 10^{-5}$	3-10	Purple
		c	5.0 ml	$2.0 \times 10^{-6}$	$1.0 \times 10^{-6}$	3-10	Brown
		d	6.0 ml	$1.0 \times 10^{-6}$	$3.0 \times 10^{-6}$	3-10	Brown
4.	Barium	a	6.0 ml	$1.0 \times 10^{-5}$	$3.0 \times 10^{-5}$	5-10	Reddish Brown
		b	5.0 ml	$2.0 \times 10^{-5}$	$1.0 \times 10^{-5}$	5-10	Reddish Brown
		c	5.0 ml	$2.0 \times 10^{-6}$	$1.0 \times 10^{-6}$	5-10	Reddish Brown
		d	6.0 ml	$1.0 \times 10^{-6}$	$3.0 \times 10^{-6}$	5-10	Reddish Brown

#### Precipitation of Lead Complex<sup>27,28,29,30</sup>

Exactly 0.1mg of (I) was dissolved in 100 ml of double distilled water. Also 0.160g of lead nitrate dissolved in water and volume made to 100 ml. pH was adjusted by adding incremental amount of sodium acetate buffer to obtain pH of 3,4,5 and 6 respectively in various experiments (Table II). The lead tetrahydroxy-p-benzoquinone complex formation was confirmed by IR spectra of the product using KBr disc method.

#### Determination of $\lambda_{\max}$ of complexes.

The U.V visible spectra of the reagent and complexes were also examined for 300 to 600 nm region and recorded but molar extinction coefficients ( $\epsilon$ ) could not be calculated due to incomplete data on stoichiometric

reactions of the reagent.

#### Atomic absorption studies.

The solutions of individual cations in aqueous medium of various concentrations, corresponding THBQ complexes and mixture of various cations containing THBQ were investigated using SP 90 A atomic absorption spectrophotometer.

The concentration versus absorbance signal was measured and statistically analyzed data is presented in table (III). The results indicate that the signal for metal – reagent system is better than for simple aqueous cation system. Also, the presence of other cations such as iron and mercury do not affect the level of copper signal and copper can be detected at its resonance line i.e.  $\lambda = 326$  nm, whereas mercury and iron resonance lines fall at 252nm and 253.7nm respectively.

Table II. Determination of stoichiometric relationship of lead tetrahydroxy-p-benzo-quinone complexes at various pH range.

S.No.	pH	Mole of lead	Mole of Reagent used	Weight of ppt (mg)	Reagent consumed	Mole Ratio of Metal	Reagent	Remarks
1.	3	$7.24 \times 10^{-5}$	$2.9 \times 10^{-4}$	23	$4.65 \times 10^{-5}$	1.55	1	At pH 3.0 the
2.	4	$7.24 \times 10^{-5}$	$2.9 \times 10^{-4}$	25	$5.81 \times 10^{-5}$	1.24	1	mole ratio of
3.	5	$7.24 \times 10^{-5}$	$2.9 \times 10^{-4}$	25	$5.81 \times 10^{-5}$	1.24	1	3:2 may be adopted
4.	6	$7.24 \times 10^{-5}$	$2.9 \times 10^{-4}$	25	$5.81 \times 10^{-5}$	1.24	1	for charged complexes.

### Results and Discussion

The organic molecule involved in complexation or chelation have roughly been grouped according to their functional groups and characteristics<sup>8,9,10,11</sup>. The most important among these systems and related to present studies are detailed as Follow:

- i.  $\beta$ -diketones, such as acetylacetone, benzoyl acetone and related compounds.
- ii. Azomethine derivatives, such as quinolines and their hydroxy or sulfur or halogen substituted derivatives.
- iii. Oximes such as dimethylgly-oxime and  $\alpha$ -benzil-dioximes.
- iv. Nitroso compounds, Pyridyl-azo compounds, thioximes, dithiozine, dithiols, semi-carbazides, carbazones, dithiocarb-amates, xanthates and many others.
- v. Some of the high molecular weight species such as flavonal, morin, naphthaquinones, diphenyl carbazides, quinon-alizarin, 1-(2-Pyridylazo)-2-naphthol, picrolinic acid and phenanthroline are also worth mentioning due to their individual chemical activity and interaction with metal ions with formation of intense colours. The use of such colour sensitive reagents has become of vital importance in a wide range of analytical and biological processes. Now-a-days great emphasis is being given to understand the mechanism of such reactions as well as make use of coloured

materials to improve limits of detection of various metals through physico-chemical measurements.

The bluish black coloured molecule of tetrahydroxy-p-benzoquinone<sup>12</sup> is dibasic. It has a violet colour in the crystalline state and is sparingly soluble in ethanol and cold water but very soluble upon heating. Substituted anions such as aniline, toluidines etc increase colour shades which are evidently due to the different portions occupied by various groups in amines. For example para and ortho toluidines produce differently coloured derivatives with (I) than meta toluidine. Similarly esters of tetrahydroxyquinones were also prepared and recrystallized as described. The formation of metal quinones had also been reported, however, elemental analysis has not been reported nor any structural elucidation accomplished previously.

The structural formula (I) of the tetrahydroxy-p-benzoquinones indicates that it can be used in various reactions.

#### *Tetrahydroxy-p-benzoquinone (I).*

The use of this reagent as a selective reagent for the determination of lead in soluble sulfate<sup>13</sup> found in soils and specific detection of barium<sup>14</sup> and strontium has been reported.

An attempt to isolate the salt rhodizonic acid<sup>15,16</sup> and the subsequent isolation of the disodium salt of (I) has been carried out by many workers.

The reactions of (I) with various metal ions have been investigated by gravimetric, volumetric and spectrophotometric methods over a wide range of pH. The re-

Table III. Slopes and intercepts of linear-graphs of absorbance versus concentration for standard aqueous solutions of copper, iron and mercury ions and their corresponding metal-tetrahydroxy-p-benzoquinone.

Metal ion	Conc. range (ppm)	Absorbance range "A"	Statistical analysis $y^* = \max + c$				
			m	c	r	$\delta x$	$\delta y$
Copper ion (aqueous)	0.0 to 50	0.0 to 0.62	0.013	0.019	0.990	17.53	0.22
Copper-THBQ complex	0.0 to 50	0.0 to 0.70	0.014	0.042	0.990	17.16	0.24
Iron ion (aqueous)	0.0 to 50	0.0 to 0.31	0.003	0.023	0.976	33.78	0.11
Iron-THBQ complex	0.0 to 100	0.0 to 0.30	0.003	0.0160	0.987	35.05	0.11
Mercury ion (aqueous)	0.0 to 100	0.0 to 0.065	0.0006	0.004	0.990	35.72	0.022
(Copper + Iron + Mercury) THBQ	0.0 to 50	0.0 to 0.64	0.013	0.009	0.996	16.94	0.22

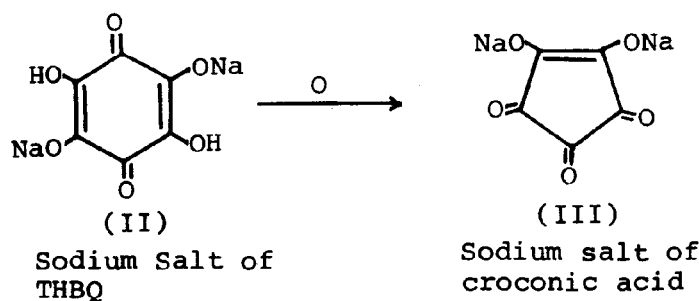
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Key: 5.0 ppm of iron and mercury respectively were present in solution but no interference in copper signal was observed.

m = Slope, c = intercept, "r" = correlation coefficient,  $\delta x$  = deviation in x-data,  $\delta y$  = deviation in y-data.

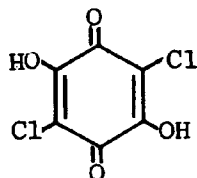
agent has been found to react with most of the metal ions but the stoichiometry of the complexes cannot be established under the experimental conditions for individual metal ion or for the mixture at different pH and dilutions.

However, Nietzki and Benkiser<sup>17</sup> described the disodium salt of (I) as a dark green, crystalline material which dissolves in water to give an orange coloured solution that yields sodium croconate on evaporation. There it is believed that this green material which was obtained may be the disodium salt<sup>18</sup> of tetrahydroxyquinone ( $C_6H_6H_2Na_2$ ).



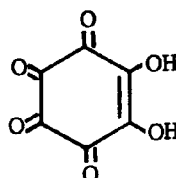
The production of characteristic colour is advantageously utilized.

- i. For the direct spectrophotometric estimation of the species giving rise to the colour.
- ii. For the detection end point e.g. by means of and indicator in acid-base or oxidation-reduction titration or by adsorption of an indicator into precipitates.
- iii. Difference in solubility may be made the basis of a gravimetric method or used for volumetric analysis or for separation of trace constituents by coprecipitation.



(IV)

Chloroanilic acid



(V)

Rhodizonic acid

- iv. The use of "Masking and Demasking" reagents to prevent species other than the one being studied from participation in a reaction.
- v. Differences in distribution between solvents at controlled pH values used in solvent extraction.
- vi. Difference in ion-exchange and chromatographic behaviour.
- vii. Difference in volatility.
- viii. Oxidation or reduction to other valence state.

From its similarity to chloranilic acid, reagent (I) should also react with metal in a similar way but the complexes should be more water soluble.

The estimation of bismuth and lead in mixtures was accomplished by different techniques, but most of the authors had applied the magnetic concentration method in past. With the passage of time the new techniques were developed and employed for separation of metals in mixture such as gravimetry, electro gravimetry, colorphotometry and the potentiometry. Though these techniques were rather costly even than there are many interfering elements such as  $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$  which need special procedures or multistage extractions and estimation. However, new techniques were useful due to their advantages like accuracy, time saving and simplicity.

In this work, the usefulness of reagent for separation of metals by complexation is investigated. In past little attention was focussed on this reagent to use it in qualitative and quantitative work. The preliminary findings reported in this work are encouraging and indicate that with little hindsight the reagent can be adopted as potential organic reagent for analysis of ores, minerals and alloys involving various gravimetric volumetric and electrometric, atomic absorption or spectrophotometric techniques.

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