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TRACE METALS ANALYSIS THROUGH EXTRACTIVE PHOTOMETRY BY COMPLEXATION WITH MONOBROMO 8-HYDROXYQUINOLINES: A REVIEW

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ABSTRACT

The analysis of the trace metals present in various chemical samples such as alloy, blood and pharmaceutical is perform through extractive photometry by complexation with monobromo 8-Hydroxyquinoline. The complexation between the metal ions presents in the samples with monobromo 8-Hydroxyquinoline gives stable chelates. These chelates quantitatively analyzed by spectrophotometry. A sensitive and selective spectroscopic method is used for the rapid determination of selected metal ions. This method allows the determination of metal ions concentration in ug mL^{-1} and features a detection limit of ng mL^{-1}. The analytes were investigate through complexation followed by extractive photometry for the detection of trace metal ions which included the interference studies, precision, accuracy, sensitivity and selectivity of the analytical methods. This method may be applied to metals in combinations. Moreover it will be useful for the further investigation and development of the 8-HQ reagents as sensing material for various trace metal ions.

Keywords: Trace metals, Extraction, Photometry, Complexation, monobromo-8-Hydroxyquinolines, Chelates.

INTRODUCTION

Metals are widely used in various industries ranging from metal works to metallic alloys, electric appliances to electronic circuitry, medicines to cosmetics, plastics to fertilizers, paints and dyes, insecticides and herbicides, etc. Each metal has its use in different ways, such as Al is important material in can industry; whilst Cr, Mn, Ni and Cu are used in alloys. Pb, Cd, Ni, and Hg are employed in battery production. Cu, Ni and Hg are found use in the electronic appliances and electrical industries. The release of metals into environment- water resourses, soil, and air- affects the ecological and human health, directly and indirectly [1].

Fe, Mg, Co, Cu, Zn and Mo are essential trace metals. In addition to this now Si, V, Cr, Ni, Se, Sn and even As have been identified as being essential elements. Some elements such as Cd, Hg and Pb are classically regarded as toxic since they have noxious effect at very low levels.

However it should be remembered that all metals are potentially toxic when the limits of their safe exposure are exceeded. In excess resulting from accidental, environmental or occupational exposure both essential and non-essential metals behaves as toxins.

Determination of these metal ions both essential and non-essential from appropriate samples can therefore provide valuable information about the health and disease causes to an individual. Beside this there is variety of fields such as environment, agriculture, pharmaceuticals, foods, and forensic sciences, where even analysis of trace amount of these heavy metals has important although the objective of such an analysis may be slightly different.

There are numerous studies have been performed on the heavy metals analysis using various organic compounds by complexation followed by extraction and instrumental investigation of metal ions. The efforts have been made mainly on the analysis of metals particularly those which have nutritional and clinical significance [2].

8-hydroxyquinoline and its derivatives form stable chelates with variety of metal ions. Since these chelates results of acidic hydrogen substitution in parent compound, they are structurally similar to 8-hydroxyquinoline itself and their properties may expected to reflect those of 8-hydroxyquinoline with suitable modifications depending upon the metal ions themselves (2).

For ex. 7-bromo-8-hydroxyquinoline was successfully used for quantitative analysis of various metal ions such as Cu(II) in common alloys, Fe(III) in blood samples, and Zn(II) in some pharmaceuticals as a complexing reagent in spectrophotometric estimation. The substitution of Bromo group at 7-postion in 8-hydroxyquinoline increases the complexing ability and sensitivity of the reagent in spectrophotometric analysis by increasing stability of complex form and absorption of light respectively [2].

Quinoline has been widely used in analytical chemistry. Because of the pyridine group present in a quinoline molecule, it forms more stable complexes with a metal ion. Recently, there are many types of quinoline derivatives that have been used by researchers for the detection of metal ions. Amongst these, 8-hydroxyquinoline is well known to react as a chelating and/or preconcentration agent with several metals because of the presence of basic nitrogen, and a phenolic group in its bonding [3].

Compared to its derivatives, HQ is very unselective. It chelates with many metals to form complexes, whereas certain derivatives of HQ only chelate with fewer metals under the same conditions. On its own, HQ is non-fluoresced and sometimes it displays very weak fluorescence due to the intramolecular proton transfer process (from oxygen to nitrogen) in its excited state, which provides a route for non-radiative relaxation [4].

Chelation of metal ions, however, can decrease the p*K*a values of the hydroxyl proton, and once this proton is lost, HQ becomes highly fluorescent [5].

Oxine (8-hydroxyquinoline) and its derivatives occupy a uniquely important place in analytical chemistry, perhaps second only to EDTA and its analogues [6].

The 8-hydroxyquinoline (oxine) behaves as a bidentate (N,O-) univalent ligand to form chelates with several metal ions. Cations with n charge and 2n coordination number form the so-called “Coordination saturated uncharged chelates” which are insoluble in water, but easily soluble in organic solvents. Owing to its great ability to form metal complexes, 8-hydroxyquinoline and its derivatives have been the subject of many studies involving analytical applications [7].

For ex. The 7-(4-nitrophenylazo)-8-hydroxyquinoline-5-sulphonic acids is use as a spectrophotometric reagent for zinc determination is selective, rapid and simple. The complex form is very stable and shows a good sensitivity in a borax buffer solution. This method was successfully applied for zinc determination in standard samples of copper-base alloys and pharmaceuticals and the results show good agreement with certified values with the results obtained by ICP-AES methods [7].

While there is a substantial amount of literature on the metal complexes of HQS, these largely do not deal with the analytical applications of it. To determine the metals in solution by complexation, extractive photometry method is widely used because of its various advantages such as low cost, eco-friendly, less time consuming, proper quantitative estimation and most important easy to operate.

It is with this approach 8-hydroxyquinoline and its derivatives have been investigated during the past several decades and the efforts are still continuing to improve the analytical applications of these ligands in solvent extraction, spectrophotometry and chromatography.

In this review, the structures, complexes form and applications of some Monobromo-8-Hydroxyquinoline in extraction of trace metal ions and its analysis by photometry will be discussed.

Monobromo-8-hydroxyquinolines:

8-Hydroxyquinoline (8-quinolinol, oxine) might be thought to function as a phenol, but of the 7 isomeric Hydroxyquinolines only oxine exhibits the capacity to chelate metals. If the hydroxyl group is blocked so that the compound is unable to chelate, as in the methyl ether, the complexing ability is destroyed. The relationship between chelation and activity of oxine are related to each others. Oxine itself is inactive, and exerts activity by virtue of the metal chelates produced in its reaction with metal ions in the medium. For ex. Its own solution has

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no particular color but when it complex with metal ions it exhibit different colors as already mentioned in the introduction.

8-Hydroxyquinoline (8-HQ) moiety has received continuous attention as a platform for the construction of a number of selective and efficient ionophores. The most interesting feature of 8-HQ is its very low quantum yield in aqueous or organic solutions but the fluorescence enhancement occurred from cation binding and many metal chelates of 8-HQ exhibit intense fluorescences. Although the selectivity of 8-HQ is rather poor, it can be improved by appropriate substitution on rings.

8-hydroxyquinoline (8-HQ) is a bicyclic compound derived from quinoline 2 (1-azanaphthalene) and consist of two rings system: carbocylic ring and pyridine ring with hydroxyl group substituted at position-8. 8-HQ has typical phenolic properties, *e.g.* it give violet colour with ferric chloride, couple with diazonium cations, and participate in Reimer-Tiemann and Bucherer reactions; its acetate ester usually undergo the Fries rearrangement with aluminium chloride to give acetyl derivative (8).

8-hydroxyquinoline forms 6 (six) monobromo derivatives (at positions 2, 3, 4, 5, 6, and 7). Among these 5 and 7 monobromo-8-hydroxyquinolines are easy to synthesis.

The presence of bromo group at 7-position in 8-hydroxyquinoline increases the analytical ability of the ligand as already mentioned in introduction of the review. It increases the complex forming ability and absorption of complex formed by the 8-HQ. Consequently enhances the sensitivity of the spectrophotometer by increasing molar absorption.

7-bromo-8-hydroxyquinoline synthesized by the published procedure (8). Its purity checked by m.p. and FTIR. The stock solution of 1×10^{-2} mol dm^{-3} was prepared by dissolving 0.224 g. of 7-bromo-8-HQ in 100mL of methanol.

Metal Complexes form by 7-Bromo-8-Hydroxyquinoline:

Complex forming (Chelating) agents are becoming of increasing importance in analytical chemistry such as in gravimetric, titrimetric and colorimetric measurements. New types of complexes and complex forming agents are constantly under investigation, for possible analytical and industrial applications. The growing importance of the use of metal chelates in analytical chemistry may be realized by the ever-increasing number of publications on this subject.

As a result of the proximity of the hydroxyl group to the heterocyclic nitrogen, 8-HQ forms insoluble chelate complexes with a great variety of metal ions, including Cu^{2+}, Bi^{2+}, Mn^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, $Zn^{2+}$and Ni^{3+}. The hydrogen of the hydroxyl group in 8-HQ is displaced and the metal is linked to both the oxygen and nitrogen. Four-covalent metal complexes therefore require two molecules of 8-HQ for each atom of metal and six-covalent metal complexes require three molecules of 8-HQ (9).

The reagent 7-bromo-8-hydroxyquinoline is water insoluble and also the complexes form by it with various metal ions. So organic solvents are needed to be use for this analysis. This reagent form stable chelates with variety of metal ions such as Cu(II), Fe(III), Zn(II), Mn(II), V(V), Co(II) at various pH in Chloroform. The absorbance of the complex abstract was found to be stable upto 12 hours. The composition of the complexes form are either 1:2 or 1:3. For ex. Cu(II), Zn(II), Mn(II) has 1:2 while Fe(III) has 1:3 ratio between Metal and Ligand respectively (10,11,12,13).

Application of 7-Bromo-8-Hydroxyquinoline as a Complexing Reagent in Trace Metals Analysis by Extractive Photometry:

As the method employed is accurate, fast and precise it can used in analysis of trace metal ions in various samples such as alloys, blood and food stuffs, pharmaceuticals, environmental samples as describe below:

Copper (II) in alloys: A method for spectrophotometric determination of Copper (II) is developed based on its extraction of the chelate complex with 7-Bromo-8-Hydroxy Quinoline at pH 3.0 into chloroform. The extract absorbs maximum at 410nm. The molar absorption was 0.156×10^{3} $dm^{3}mol^{-1}cm^{-1}$. Beers law obeyed from 0.8 to 7.2 ppm of copper. The absorbance of the abstract remains stable up to 12 hours. The composition of the abstracted complex is 1:2. The method is applied for the determination of copper in some copper based alloys such as brass and white metal etc (10).

Iron (III) in blood and food stuffs: The food stuffs (rice, wheat flour, banana, tomato) were oven dried at 90˚C for 24 hrs. A 5g sample (or 10mL of human blood) was digested with 10mL of acid mixture of HNO_3, H_2SO_4 and $HClO_4$ (3:1:1) mixture was evaporated to dryness. The residue dissolved in 5mL of slightly acidified water by heating. The solution transferred quantitatively into 100 mL volumetric flask and made upto the mark with distilled water. The extraction is performed using 7-Bromo-8-hydroxyquinoline in chloroform at pH 5. Complex gives a pale yellow color having high absorbance at 320nm maxima. The method has been applied satisfactorily applied for determination of Iron (III) in blood and food stuffs (11).

Zinc (II) in Pharmaceuticals: The spectrophotometric determination of zinc (II) performed by extracting its chelates with 7-bromo-8-hydroxyquinoline at pH 9.0 into chloroform. The absorbance is stable up to 15 hrs. The Beers law is obeyed in the range of 0.8 to 4.8 ppm of Zinc (II). The recommended procedure was employed for 10 replicate determination of 4 ppm of Zn (II). The relative standard deviation was found to be 1.8 % and it varies from the mean at 95 % confidence limit was found to be 4.0 + and – 0.123 ug of Zinc (II) (12).

Manganese in some environmental samples: The method has been applied for the determination of Mn (II) in some environmental samples such as various fish samples marketed in fish markets in Mumbai coastal area and found that the method is suitable. Mn (II) extracted as a 7-bromo-8-hydroxyquinoline chelates at pH 8.0 into chloroform. The extract absorbs maximum at 390 nm and it is stable up to 16 hrs. The Beers law obeyed in the absorbance range of 300-500nm between 0.8 to 6.4ppm of Mn(II). The composition of the complex form is found to be 1:2 by molar ratio method (13).

For all these experiments performed a shimadzu UV/60 of visible spectrophotometer with quartz cell of the 1 cm path length and control dynamic digital pH meter with combined glass electrode were used for absorbance and measuring the pH of the solutions respectively (9,10,11,12,13).

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CONCLUSION

7-bromo-8-hydroxyquinoline can be use as a complexing agent for various trace metal ions in the field of alloy industries, health, pharmaceuticals, and environment through extractive photometry.

This method (extractive photometry) could be suitable for quality control laboratories for analysis of various metal ions present in environment samples, pharmaceuticals, agriculture, food industries and forensic sciences because the methods will not require separation steps and the instrument used is relatively not expensive and sophisticated.

Also it will be useful for the further investigation and development of the HQ reagents as sensing material for various metal ions.

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