

Solvent Extraction and Spectrophotometric Determination of Magnesium by Paratoly 1-2-Thenohydroxamic Acid and Quinalizarin

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ABSTRACT: Magnesium is extracted with a chloroform solution of *N-p-tolyl-2-thenohydroxamic acid (PTTHA)* from aqueous solution of pH 9.5. *Mg-PTTHA* complex is colourless and the colour is developed by adding quinalizarin into the extract. λ_{max} and ϵ of the complex are 590nm and $2.8 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$ respectively.

Most common ions do not interfere in the determination of magnesium. The spectral characteristics of magnesium complexes with hydroxamic acids are recorded. Magnesium is also determined by AAS and the results are in agreement with those of spectrophotometric method. The method is applied to the determination of magnesium in standard alloy samples.

KEY WORDS: Hydroxamic acid, Magnesium, Extraction spectrophotometry.

INTRODUCTION

Different magnesium compounds like citrate, oxide, sulfate, carbonate, are used as antacids; Magnesium alloys are used in aircraft, photographic and optical equipments for its low density (1.74 gcm^{-3}). It is used for cathodic protection of other metals from corrosion as a scavenger. Up to 5% Mg is added to Al to improve its mechanical and weldability properties and corrosion resistance [1].

Several reagents have been reported for the spectrophotometric determination of magnesium, like: Eriochrome Blak T method, which requires precise pH

adjustment for analysis of sample and standard solutions. The sensitivity of the assay depends upon the ionic strength. Elements of Ca and group I-III metals interfere with the determination and must be removed beforehand. Titan yellow method, although has a high molar absorptivity of $3.6 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$ suffers from the problem that the intensity and reproducibility of the colour are affected by the pH, excess reagent, time of standing and the temperature of the solution. Extractive-spectrophotometric method with 8-hydroxyquinoline in the presence of butylamine is reported with molar

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absorptivity of $7.0 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$ at 388nm [2-5].

The method described in this paper has the following features. It is rapid, selective, independent of temperature change, colour is stable for at least 24 hours.

Hydroxamic acids are versatile and important ligands in analytical chemistry which may be used in determination of several metal ions by different methods [6-10]. To study the extractive behavior of these ligands towards alkaline earths in the present investigation a method has been developed for the extraction and spectrophotometric determination of magnesium with N-p-tolyl-2-theno hydroxamic acid (PTTHA).

EXPERIMENTAL

Chemicals and Reagents

All chemicals were of Analar or G.R. grades from Fluka (Buchs, Switzerland) and Merck (Darmstadt, Germany). Hydroxamic acids were synthesised by reacting hydroxylamines with 2-carboxylic acid-chlorides [11]. Their purity was established by MP, elemental analysis, NMR, UV and IR spectroscopy. A $6.4 \times 10^{-4} \text{ M}$ solution of the hydroxamic acid in chloroform was used for extractions. A 0.01% (w/v) quinalizarin (I) solution in ethanol was used for colour development.

Double distilled deionized water was used throughout. Spectroscopic grade ethyl alcohol was used for the preparation of quinalizarin solution.

Chloroform (Fluka) was purified by method of Weissberger [12], Buffer solutions of pH 6-11 were prepared as per NBS standard [13].

A stock solution of magnesium perchlorate was prepared by treating 0.25 gr pure MgCO_3 with perchloric acid and diluting up to 250 ml with water, the concentration of metal ion ($9.9 \times 10^{-3} \text{ M}$) was determined with EDTA solution (0.01M) [14]. Working solutions

were obtained by appropriate dilution of the stock solution.

Apparatus

An Elico model LI-120 digital pH meter was used for the pH measurements. Absorbance measurements were made with a Shimadzo (Japan) UV-Visible, model UV 160 spectrophotometer.

A GBC 901 atomic absorption spectrometer, employing the 202.6 nm magnesium line and nitrous oxide-acetylene flame, was used for atomic absorption (AA) measurements. A magnesium hollow-cathode lamp operated at 3.5 mA with a band pass 0.5nm, was used as the light source.

Procedure

An aliquot of the sample solution containing 6.0-100 $\mu\text{g/ml}$ of Mg^{2+} was placed in a 10ml volumetric flask. 5ml buffer solution of pH 9.5 was added and the solution was diluted to the mark with distilled water. This solution was transferred into a 60ml separatory funnel. 10ml of $6.4 \times 10^{-4} \text{ M}$ PTTHA solution in chloroform was added and the mixture shaken vigorously for 10 min, after the phase separation the organic extract collected. To ensure the complete recovery, extraction was repeated with 5ml PTTHA, the organic layer dried over anhydrous sodium sulphate then washed sodium sulphate with 2ml chloroform. The extracts and washing were transferred into a 25 ml volumetric flask; 4 ml of quinalizarin solution was added to develop the colour, then diluted the mixture with chloroform upto the mark. The absorbance of bluish-violet complex was measured at 590 nm against the reagent blank.

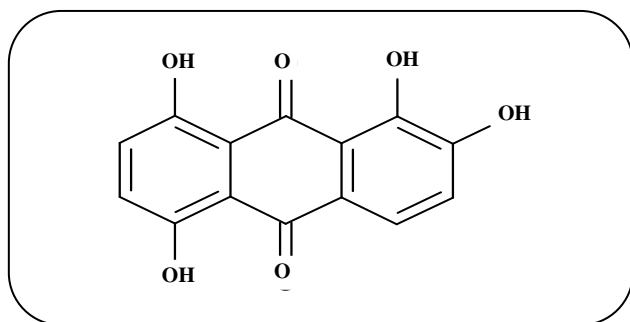
For AA spectroscopy, the chloroform extract was stripped with 0.01M HCl. The values of percentage extraction (%E) and distribution ratio (D) of magnesium were calculated at different pH and PTTHA concentrations.

RESULTS AND DISCUSSION

A comparison of the sensitivity of reaction between magnesium and different hydroxamic acids is shown in table 1, where PTTHA indicates more sensitivity, hence it was selected as the suitable ligand.

Absorption Spectra

The colourless chloroform extract of magnesium



(I)

PTTHA-complex reacts with Quinalizarin to yield bluish-violet complex with maximum absorbance at 590nm.

Effect of pH

The percentage of extraction and formation of Mg-PTTHA chelate is influenced by the pH of the solution.

Maximum extraction of magnesium with PTTHA was obtained in the pH range of 9.0-10.0, while at lower and higher pHs the yield decreased (Fig.1), which may be attributed to the hydroxide formation above pH 10 and the incomplete equilibration of ligand at pH lower than 9.0 because of its relative low dissociation constant ($pK_a = 11.15$). Hence all the extractions were carried out at pH 9.5.

Effect of PTTHA Concentration

The influence of PTTHA concentration was studied by extraction of magnesium ($8.22 \times 10^{-5}M$) with various amounts of PTTHA, keeping the quinalizarin concentration (0.01%) and the pH constant.

It was observed that $5.1 \times 10^{-4}M$ PTTHA solution is adequate for complete extraction of magnesium. Lower concentrations of PTTHA reduces the percentage of extraction, while an excess of the reagent solution can be used without any difficulty. (Table 2).

Effect of Quinalizarin Concentration

Magnesium was extracted with PTTHA into chloroform at pH 9.5 and the effect of quinalizarin on the yield of extraction was studied. Magnesium forms a colourless complex with PTTHA. The addition of quinalizarin causes a bathochromic shift, and the resulting complex shows a maximum absorption at 590nm. Various amounts of quinalizarin solution in ethanol were added to the magnesium hydroxamate and it was observed that 4ml of 0.01% solution of quinalizarin is adequate for the complete complexation and maximum absorbance (Table 3).

Magnesium in the aqueous phase was determined by AAS and in the organic phase by spectrophotometry.

Calibration Graph and the Optical Properties

The bluish-violet magnesium - PTTHA - quinalizarin chelate system obeys the Beer's law in the concentration range of $0.6 - 10.20 \mu g ml^{-1}$ of magnesium, it has the molar absorptivity of $2.8 \times 10^3 L mol^{-1} cm^{-1}$ and Sandell's

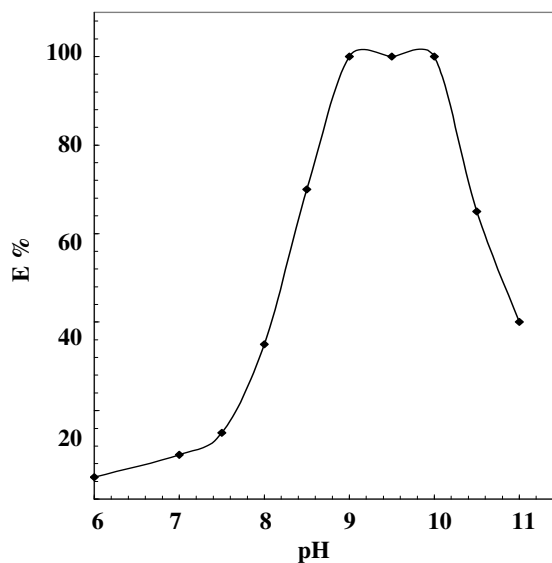


Fig. 1: Effect of variation of the pH on extraction of magnesium - PTTHA complex.

sensitivity is $0.0087 \mu g cm^{-2}$ of magnesium for 0.001 absorbance unit. Precision and accuracy of the method was studied the relative standard deviation and relative error of eight replicate measurements for $2.0 \mu g ml^{-1}$ of magnesium was 3.07% and 2.5% respectively. The results are reproducible.

Stoichiometry of the Complex

The composition of magnesium - PTTHA-quinalizarin complex extracted into chloroform has been studied by slope ratio method [15,16] i.e by plotting the graph of logarithm of the distribution coefficient of the metal $\log D_M$ against the logarithm of ligand concentration, $\log [Ligand]$. Two sets of extractions were carried out. (a) by taking a fixed amount of magnesium and quinalizarin solution and varying the concentration of PTTHA. (b) by taking a fixed amount of PTTHA and magnesium while varying the concentration of quinalizarin. The graph of $\log D_M$ against $\log [PTTHA]$ and $\log D_M$ against $\log [quinalizarin]$ gave two straight lines of slope 0.91 and 1.08 respectively which indicates that the composition of the ternary complex, Mg: PTTHA: QH is 1: 1: 1. (Fig.2-3).

The possible reactions are:

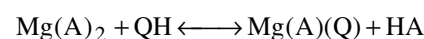
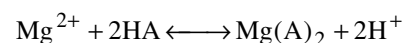


Table 1: Extraction of magnesium with different hydroxamic acids

Compound No.	Hydroxamic acid	λ_{\max}	Molar absorptivity $\text{Lmol}^{-1} \text{cm}^{-1}$	Sandell sensitivity $\mu\text{g cm}^{-2}$
I	N-Phenyl-2-Furo-	590	1.8×10^3	0.0135
II	N-Phenyl-2-Theno-	590	2.1×10^3	0.0118
III	N-P-Tolyl-2-Theno-	590	2.8×10^3	0.0087

Hydroxamic acid: 10ml, $6.4 \times 10^{-4} \text{M}$

Magnesium: 2.0 ppm

Solvent: Chloroform

Quinalizarin: 4ml, 0.01%

pH: 9.5

Table 2: Effect of varying the concentration of PTTHA on the extraction of Mg-PTTHA-Q complex

PTTHA ($\text{M} \times 10^{-4}$)	-log[PTTHA]	Magnesium conc.(M)		log D_M
		$[\text{Mg}]_{\text{org}} \times 10^{-5}$	$[\text{Mg}]_{\text{aq}} \times 10^{-5}$	
1.6	3.79	6.24	1.98	0.5
2.5	3.57	6.87	1.35	0.71
3.8	3.42	7.37	0.85	0.94
5.1	3.29	8.17	<0.05	>2.21
6.4	3.19	8.17	<0.05	>2.21

Magnesium = $8.22 \times 10^{-5} \text{M}$

Quinalizarin = 4ml (0.01%)

Solvent = Chloroform

 $\lambda_{\max} = 590 \text{nm}$

pH = 9.5

Table 3: Effect of varying the concentration of Quinalizarin on the extraction of Mg-PTTHA-Q complex

Quinalizarin ($\text{M} \times 10^{-4}$)	-log[Q]	Magnesium conc.(M)		log D_M
		$[\text{Mg}]_{\text{org}} \times 10^{-5}$	$[\text{Mg}]_{\text{aq}} \times 10^{-5}$	
1.99	3.70	6.4	1.81	0.55
2.45	3.61	6.71	1.51	0.65
2.80	3.55	6.90	1.32	0.72
3.4	3.46	7.05	1.17	0.82
3.67	3.43	8.17	<0.05	>2.21

Magnesium = $8.22 \times 10^{-5} \text{M}$ PTTHA = 10ml, $5.1 \times 10^{-4} \text{M}$

Solvent = Chloroform

 $\lambda_{\max} = 590 \text{nm}$

pH = 9.5

A possible mechanism and formula is given in Fig. 4. [17].

Effect of Diverse Ions

In order to evaluate the sensitivity and selectivity of the method, a fixed concentration of magnesium ($2.0 \mu\text{g ml}^{-1}$) was taken in the presence of a number of foreign ions and the interferences studied by measuring the absorbance of extracted chloroform phase. The ion which alters the recovery of magnesium by more than $\pm 2.0\%$ is considered as interfering ion. The results are summarized in table 4.

Determination of Magnesium in Alloy Samples

The samples were treated with mixture of perchloric and nitric acids, and evaporated to dryness. About 10ml of (50%) hydrochloric acid was added and heated until the fumes of hydrochloric acid is ceased.

The residues were leached with about 25ml of distilled water. The solution was filtered, washed with hot water, cooled and made up to 100ml with double distilled water in a calibrated flask. An aliquot of the solution was pipeted out and the magnesium content was determined by the prescribed procedure. The results are given in table 5.

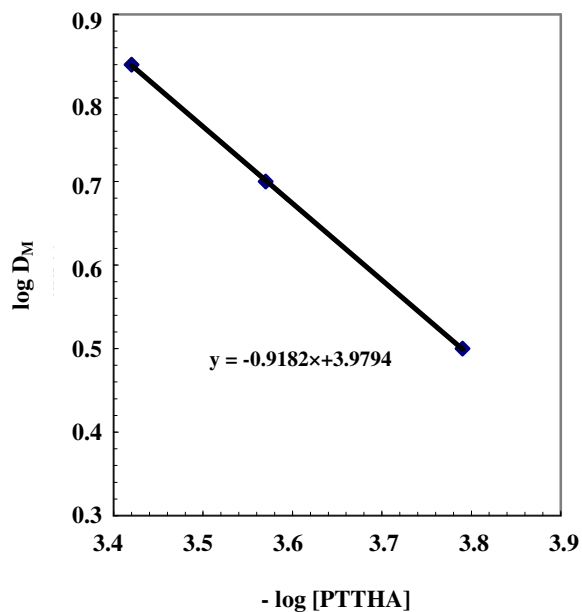


Fig. 2: Distribution ratio of magnesium [DM] vs hydroxamic acid [PTTHA].

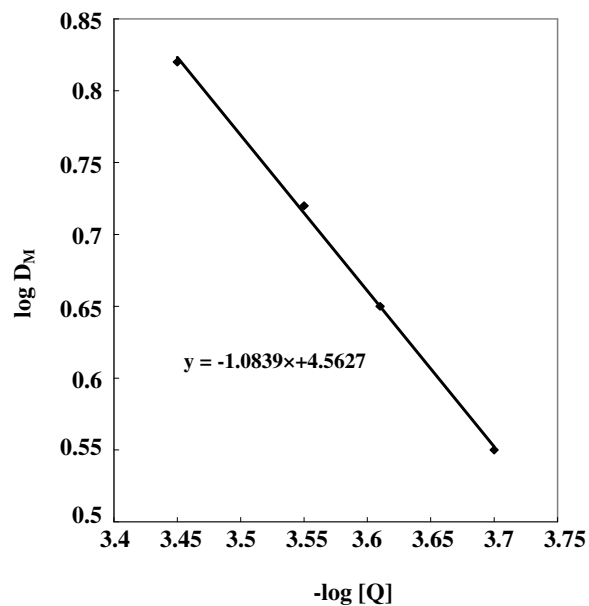


Fig. 3: Distribution of magnesium [D_M] vs quinalizarin [Q]

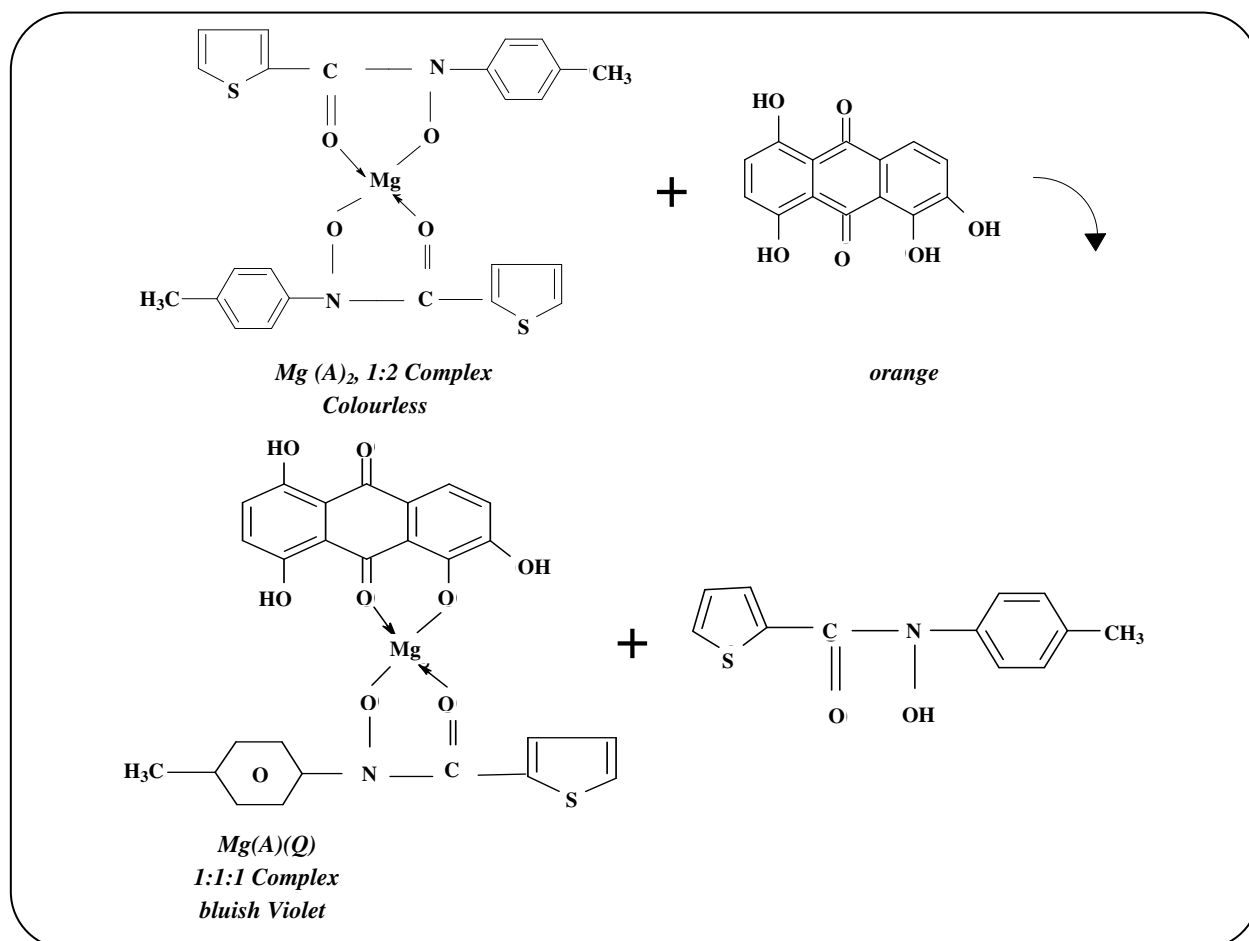


Fig. 4: The possible mechanism and formula

Table 4: Separation of Magnesium from its binary mixtures

Diverse ion	Added as	Amount added ppm	Recovery of Mg(%)
Al ³⁺	AlCl ₃	50	98.5
Ga ³⁺	GaCl ₃	45	98
Ca ²⁺	CaCl ₂	30	98.2
Be ²⁺	BeCl ₂	35	98.5
Sr ²⁺	SrCl ₂ .6H ₂ O	40	98.5
Ba ²⁺	BaI ₂ .7H ₂ O	40	98.9
Co ²⁺	Co(NO ₃) ₂ .6H ₂ O	50	98.7
Zr ⁴⁺	Zr(NO ₃) ₄ .5H ₂ O	35	99
Ti ⁴⁺	TiCl ₄	35	99
Hg ²⁺	HgCl ₂	40	98.2
MoO ₄ ²⁻	Na ₂ MoO ₄	50	99
UO ₂ ²⁺	UO ₂ (NO ₃) ₂ .6H ₂ O	40	98.5
K ⁺	KCl	50	99
Na ⁺	NaCl	50	99
Ag ⁺	AgNO ₃	40	98.8
Bi ³⁺	Bi(NO ₃) ₃ .5H ₂ O	50	98.7
Th ⁴⁺	Th(NO ₃) ₄ .5H ₂ O	50	98.6
Tl ³⁺	Tl(NO ₃) ₃	50	98
Cu ²⁺	Cu(NO ₃) ₂	40	97.8
Br ⁻	KBr	50	98.9
I ⁻	KI	45	99
CH ₃ COO ⁻	NaC ₂ H ₃ O ₂	45	98.9
C ₂ O ₄ ²⁻	Na ₂ C ₂ O ₄	40	94
SCN ⁻	NaSCN	40	99
NO ₃ ⁻	NaNO ₃	40	98.9
EDTA	Na ₂ H ₂ Y	30	95.3

Magnesium: 2.0 ppm

Quinalizarin: 4ml, 0.01%

PTTHA: 10ml of 6.4 × 10⁻⁴Mλ_{max}: 590nm

Solvent: Chloroform

pH: 9.5

Conditions: Mg separated (a) from the cations, Al³⁺, Be²⁺, Ga³⁺, Ti⁴⁺, UO₂²⁺ and Zr⁴⁺ in presence of NaF(5 × 10⁻³M).(b) from the cations, Sr²⁺, Cu²⁺, Ba²⁺, Th⁴⁺, Co²⁺, Hg²⁺ in presence of EDTA (5 × 10⁻³M).(c) from the cations, Tl³⁺, Bi³⁺ in presence of KI(5 × 10⁻³M).

Table 5: Determination of magnesium in standard alloy samples

sample	certified Value of Mg %	Mg found			
		A A S		spectrophotometry	
		Mg%	RSD%	Mg%	RSD%
Al-Mg alloy (BSH ₄)	2.25	2.26	0.03	2.23	0.05
Al-Mg-Si alloy (BSH ₁₅)	1.00	0.98	0.05	1.03	0.07
Al-Cu-Mg alloy (BSH ₃₀)	1.50	1.52	0.04	1.48	0.05

Results are average of seven determinations.

BS - British standard sample

RSD - Relative standard deviation

US - American standard sample.

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