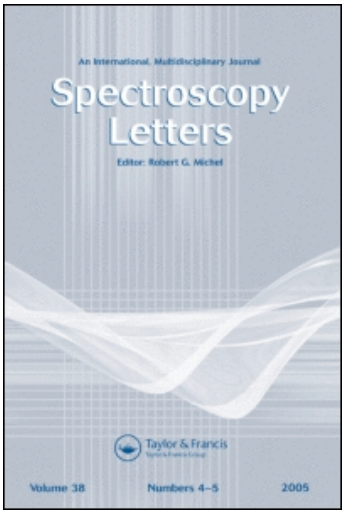


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

1-(2-Quinolylazo)-2,4,5-trihydroxybenzene as a Reagent for the Spectrophotometric Determination of Nickel(II) and Lead(II)

Radi Salim[a]; A. H. Laila[b]
[a] Chemistry Department, An-Najah University, Nablus, West Bank, Israel [b] Chemistry Department, Birzeit University, West Bank, Israel

To cite this Article Salim, Radi and Laila, A. H.(1986) '1-(2-Quinolylazo)-2,4,5-trihydroxybenzene as a Reagent for the Spectrophotometric Determination of Nickel(II) and Lead(II)', Spectroscopy Letters, 19: 6, 669 — 679
To link to this Article: DOI: 10.1080/00387018608069271
URL: http://dx.doi.org/10.1080/00387018608069271

SPECTROSCOPY LETTERS, 19(6), 669-679 (1986)

1-(2-QUINOLYLAZO)-2,4,5-TRIHYDROXYBENZENE AS A REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF NICKEL(II) AND LEAD(II)

Key words: Spectrophotometry, Pb-QATB, Ni-QATB

Radi Salim* and A.H. Laila**

* Chemistry Department, An-Najah University, Nablus, West Bank, via Israel

** Chemistry Department, Birzeit University, Birzeit, West Bank, via Israel

ABSTRACT

The reagent 1-(2-Quinolylazo)-2,4,5-trihydroxybenzene (QATB) has been used for developing a method for the spectrophotometric determination of nickel (II) and lead (II). Variables influencing the sensitivity of this method such as wavelength, pH and time have been investigated. The limitations of this method and the effect of interfering ions have also been investigated. Few properties of the complexes formed between QATB and metal ions (Ni and Pb) such as composition, stability and free energy of formation have been determined.

0038-7010/86/1906-0669$3.50/0

INTRODUCTION

The toxicity of both lead ions and nickel ions has been known for several years[1]. Understanding and controlling the toxicity effects of these ions require the development of sensitive methods of determination for these elements. In this aspect the visible and UV spectrophotometric methods of analysis have the advantage of being simple and sensitive.

Several reagents have been suggested for the determination of lead (e.g. dithizone[2], 4-(2-pyridylazo)resorcinol[3], Arsazen[4], 2-(5-bromopyridylazo)-5-diethylaminophenol[5] and 3-methyl-1,2-cyclopentadione dithiosemicarbazone[6]) and for the determination of nickel (e.g. dimethylglyoxime[7], α-furildioxime[8], 2-(2-thiazolylazo)-5-dimethylaminophenol[9], 4-(2-pyridylazo)thymol[10] and 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol[11]). The aim of this paper is to introduce a new reagent, 1-(2-quinolylazo)-2,4,5-tryhydroxybenzene (QATB), for the spectrophotometric determination of lead and of nickel and to study the complexes of these elements with the reagent QATB.

EXPERIMENTAL

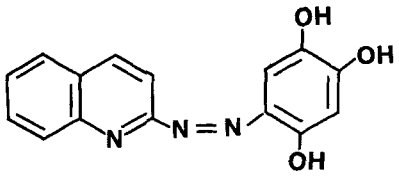
APPARATUS

A Bausch and Lomb 2000 Spectronic UV Spectrophotometer was used for recording the absorption spectra. A Corning pH-meter, Model 140, was used for the pH measurements.

REAGENTS

The QATB reagent was prepared by refluxing equimolar amounts of 2-hydrazinoquinoline (dissolved in dilute HCl) and 2,5-dihydroxy-1,4-benzoquinone (dissolved in ethanol) for one hour. Ammonium hydroxide was added and the excess of ammonia was then boiled off. The product was then precipitated as brown solid and when recrystallized it turned to a dark red product with a melting point of 275°C. The structure of

this reagent is shown below[12]:



A stock solution of 2 x 10^{-3} M of the reagent QATB was prepared by dissolving the proper amount in 95% ethanol. Stock solutions of lead and of nickel ions were prepared by dissolving the proper amounts of the nitrate salt of each metal in distilled water.

The buffer solutions used were:
HCl-KCl mixtures for pH values below 2.0,
HCl-KHP mixtures for pH values between 2.0 and 4.0,
KHP-NaOH mixtures for pH values between 4.0 and 6.0,
KH_2PO_4-NaOH mixtures for pH values between 6.0 and 8.0,
Borax-HCl mixtures for pH values between 8.0 and 9.0,
Borax-NaOH mixtures for pH values between 9.0 and 10.8,
KCl-NaOH mixtures for pH values above 10.8.
All pH values used for studying the effect of pH on absorption spectra were determined experimentally after preparation and immediately before use.

All solutions were prepared from ANALAR grade reagents.

RECOMMENDED PROCEDURE

Transfer a sample containing not more than 25 µg of nickel or 150 µg lead into a 10 ml standard flask. Add 2.5 ml of buffer solution (pH 11.0 in case of nickel analysis and pH 10.5 in case of lead analysis) and then add 2.5 ml of 0.002 M QATB solution and 2.5 ml pure ethanol. Dilute to volume with distilled water and shake well. After 40 min in the case of nickel analysis or 55 min in the case of lead analysis measure the absorbance of the complex formed at 585 nm or at 610 nm for Ni-QATB

and Pb-QATB, respectively. Use 1-cm cell and read absorbance against a reagent blank. Compare the measured absorbance with preconstructed calibration curves in the range 0-2.5 μg/ml of nickel or 0-15 μg/ml of lead to determine the concentration of nickel or lead in solution.

RESULTS AND DISCUSSION

ABSORPTION SPECTRA

The absorption spectra of the ligand QATB and its complexes with Ni^{2+} and with Pb^{2+} are shown in Fig. 1. The results of this figure show that the maximum absorption of the free ligand is at 420 nm, of Ni-QATB complex is at 585 nm. These results show also that the absorption of lead gives two broad maxima at ≃ 540 and at ≃ 610 nm.

From the above it can be concluded that the suitable wavelength for the determination of Ni^{2+} is at 585 nm. At this wavelength the absorption of the free ligand is negligible. The best wavelength for the determination of Pb^{2+} is at 610 nm where no absorption from the free ligand interferes. Using the wavelength of the other maximum of absorption of Pb-QATB complex (i.e. 540 nm) is not suitable because of the high absorption of the free ligand at this wavelength.

COMPOSITION OF THE COMPLEXES

The composition of the complexes was determined by applying the continuous variation method and the molar ratio method. Both methods indicated the formation of 1:3 complexes of metal ion: ligand ratio for both Ni^{2+} and Pb^{2+} complexes with QATB.

THE EFFECT OF pH

The effect of pH on the formation of the Ni-QATB and the Pb-QATB complexes is shown in Fig. 2. The results show that in acidic pH range these complexes were not formed. In the alkaline pH range there was a

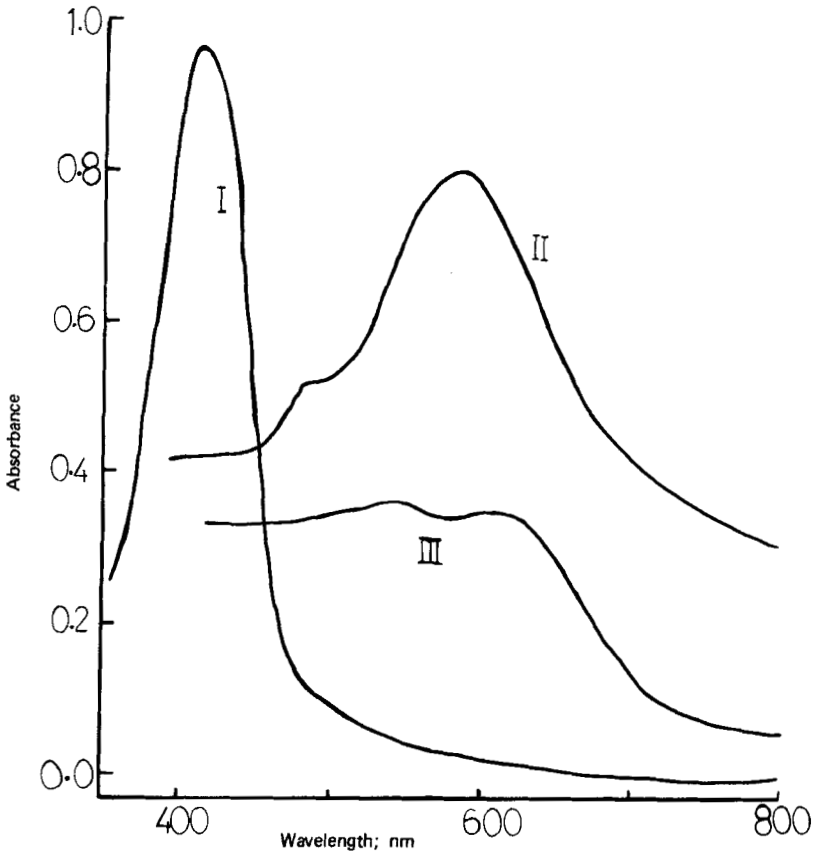


Fig. 1. Absorption spectra of: (I) QATB - $5X10^{-5}$ M.
(II) Ni-QATB complex. ligand conc. = $5X10^{-4}$ M; nickel conc. = $1X10^{-4}$M.
(III)Pb-QATB complex. ligand conc. = $5X10^{-4}$ M; lead conc. = $1X10^{-4}$ M.

great influence of pH on the formation of the two complexes with a maximum color development of Ni-QATB complex occurring at pH 11.0 and of Pb-QATB complex occurring at pH 10.5.

From the above it can be concluded that for getting the maximum sensitivity the nickel ions should be determined at pH 11.0 and the lead ions should be determined at pH 10.5.

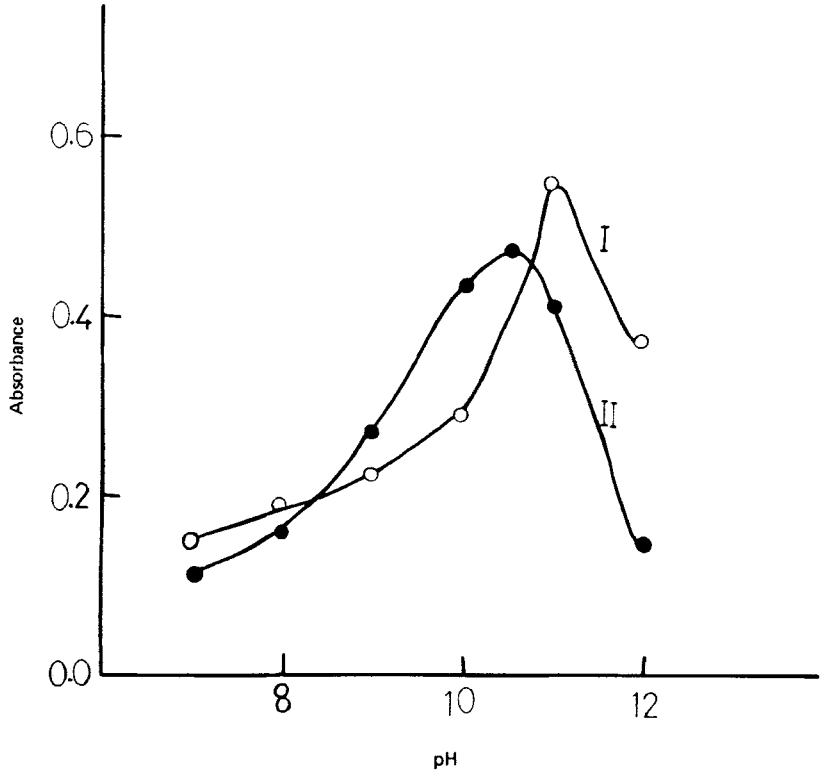


Fig. 2. Effect of pH on complex formation:
(I) Ni-QATB complex; Ni^{2+} conc. = $5X10^{-5}$ M, QATB conc. = $5X10^{-4}$ M.
(II) Pb-QATB complex; Pb^{2+} conc. = $1X10^{-4}$ M, QATB conc. = $5X10^{-4}$ M.

STABILITY OF THE COMPLEXES

QATB forms bluish red complexes with Ni^{2+} and with Pb^{2+}. The color of the Ni-QATB complex develops fully within 40 min and remains stable up to twelve hours. The color of the Pb-QATB complex develops fully within 55 min and remains stable up to twelve hours.

The average value of the apparent stability constant (β) was determined from the results of the molar ratio and the continuous variation

methods and found to be 2.39×10^{11} for the Ni-QATB complex and 2.98×10^{11} for the Pb-QATB complex. The free energy change of formation of the complexes were calculated using the relation $\Delta G^{o} = - RT \ln \beta$ and were found to be - 15.67 and - 15.54 K cal/mol for the Ni-QATB complex and for the Pb-QATB complex, respectively.

BEER'S LAW AND MOLAR ABSORBTIVITY

Measuring the absorbance of standards of Ni^{2+} solutions at pH 11.0 using the wavelength of 585 nm gave a straight relationship between absorbance and nickel concentration, in accordance with Beer's law, in the range 0 - 2.5 μg/ml.

Measuring the absorbance of standards of Pb^{2+} solutions at pH 10.5 using the wavelength of 610 nm gave the range 0-15 μg/ml as a range for application of Beer's law.

The average molar absorptivity (ε) of the complexes was calculated using the linear portion of Beer's law plots and found to be 1.79×10^{3} and 4.34×10^{3} liters.mol^{-1}. cm^{-1} for Ni-QATB and for Pb-QATB complexes, respectively.

THE EFFECT OF FOREIGN IONS

Several ions were investigated for their interferences with the formation of Ni-QATB and Pb-QATB complexes. This was done by measuring the absorbance of complex in presence of 200:1 ratio of foreign ion:metal ion. The concentration of Ni^{2+} used was 2×10^{-4} M and the measured absorbance for this concentration was 0.49. The concentration of Pb^{2+} used was also 2×10^{-4} M and the measured absorbance for this concentration was 0.25. The deviations in the absorbance reading caused by the presence of foreign ions are given in Table 1.

From the above results it can be concluded that: (i) most of the common cations such as the alkali and alkaline earth metals (except potassium)

TABLE 1

The Effect of Foreign Ions on the Absorbance of Ni-QATB and of Pb-QATB complexes

Cation	Deviation in absorbance of complex		Anion	Deviation in absorbance of complex	
	Ni-QATB	Pb-QATB		Ni-QATB	Pb-QATB
Al^{3+}	- 0.25	- 0.16	Br^-	0.00	0.00
Ba^{2+}	0.00	0.00	CH_3COO^-	0.00	0.00
Ca^{2+}	0.00	0.00	Cl^-	0.00	0.00
Cd^{2+}	0.00	0.00	CO_3^{2-}	0.75	1.46
Ce^{3+}	0.00	0.00	$C_2O_4^{2-}$	ppt	ppt
CO^{2+}	0.00	0.00	HPO_4^{2-}	- 0.05	0.27
Cr^{3+}	0.44	0.51	I^-	0.00	0.00
Cu^{2+}	0.05	0.25	NO_2^-	0.00	0.00
K^+	0.48	0.12	NO_3^-	0.28	0.18
La^{3+}	- 0.10	- 0.02	SO_4^{2-}	0.00	0.00
Mg^{2+}	0.00	0.00	SO_3^{2-}	0.00	0.00
Mn^{2+}	+ 0.26	- 0.06			
Na^+	0.00	0.00			
Ni^{2+}	-	- 0.06			
Pb^{2+}	0.01	-			
Zn^{2+}	- 0.19	- 0.08			
Y^{3+}	- 0.18	- 0.08			

do not interfere with the formation of both Ni-QATB and Pb-QATB complexes, *(ii)* potassium ion interferes highly with the formation of both complexes and should be avoided during the determination of Ni^{2+} or Pb^{2+}, (iii) other cations such as Cr^{3+}, Al^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Y^{3+} also interfere with the formation of both complexes and should be avoided during the determination of Ni^{2+} or Pb^{2+}, (iv) all common anions except CO_3^{2-}, HPO_4^{2-} and NO_3^- anions do not interfere with the determination of nickel or lead.

COMPARISON WITH OTHER REAGENTS

The reagent QATB provides a method for the spectrophotometric determination of nickel and lead in aqueous solutions. This method is simple, direct, and sensitive enough for determining traces of nickel or lead in solution. Although the sensitivity of the present method is not the best amongst the spectrophotometric methods using other reagents for the determination of lead or nickel but it is still more sensitive than several reagents used for this purpose. In addition, this method has the advantage of not requiring extraction. This avoids several problems of extraction which accompany the use of many of the more sensitive spectrophotometric reagents used for the determination of nickel or lead in solution.

CONCLUSIONS

The reagent QATB is a useful and sensitive reagent for the spectrophotometric determination of both Ni^{2+} and Pb^{2+}. It forms bluish red complexes with either Ni^{2+} or Pb^{2+}. These complexes become stable after 40 min in the case of Ni-QATB complex and after 55 min in the case of Pb-QATB and both complexes stay stable after that for at least up to twelve hours.

For maximum sensitivity the pH used for the determination of Ni^{2+} should be 11.0 and the wavelength used should be 585 nm. The pH used for

the sensitive determination of Pb^{2+} should be 10.5 and the wavelength should be 610 nm.

Beer's law is applicable, using the present method, in the range 0-2.5 μg/ml for Ni^{2+} and 0-15 μg/ml for Pb^{2+}. The average molar absorptivity (ε) of the Ni-QATB complex is 1.79×10^3 and of Pb-QATB is 4.34×10^3 liters. mol^{-1}. cm^{-1}.

Both Ni^{2+} and Pb^{2+} complexes with QATB are formed in the ratio 1:3 of metal ion:ligand. The average apparent stability constants (β) of the formed complexes are 2.39×10^{11} and 2.98×10^{11} for Ni-QATB and Pb-QATB, respectively. The free energy change of formation (ΔG^o) of the complexes are - 15.67 and - 15.54 K cal/mol for Ni-QATB and Pb-QATB, respectively.

The Reagent QATB forms colored complexes with a number of ions and these interfere with the determination of Ni^{2+} or Pb^{2+}. These ions include K^+, Cr^{3+}, Al^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Y^{3+}, CO_3^{2-}, HPO_4^{2-}, and NO_3^-. All other common cations and anions do not interfere with the determination of nickel or lead when the foreign ion is present in up to two hundred folds of concentration of Ni^{2+} or Pb^{2+}.

REFERENCES

[1] P.B. Hammond and R.P. Beliles, in *Casarett and Doull's toxicology - the basic science of poisons*, 2nd Ed., McMillan Publishing Co., New York (1980), p. 415-421, 452.

[2] J.C. Gage; *Analyst* 82, 453 (1957).

[3] A.A. Yadav and S.M. Khopkar; *Talanta* 18, 833 (1971).

[4] A.M. Lukin, L.S. Chernaya, G.S. Petrova and A.I. Sosnina; *Zavodsk. Lab.* 28, 398 (1962).

[5] S.I. Gusev and E.M. Nikolaeva; *Zh. Analit. Khim.* 24, 1674 (1969).

[6] A.H. Laila and R. Salim; *Spec. Lett.* 18, 583 (1985).

[7] W. Nielsch; *Z. Metallk.* 50, 234 (1959).

[8] A.L. Wilson; *Analyst* 93, 83 (1968).

[9] K. Kasiura and Z. Sytniewska; *Chem. Anal. (Warsaw)* 13, 177 (1968).

[10] T.M. Mirzakasimov, K.Z. Rakhmatullaev and S.T. Talipov; *Uzb. Khim. Zh.* 29, 12 (1968).

[11] F.S. Wei, P.H. Qu, N.K. Shen and F. Yin; *Talanta* 28, 189 (1981).

[12] I. Singh and Mrs. Poonam; *Talanta* 31, 109 (1984).

Date Received: 01/23/86
Date Accepted: 02/24/86