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PYRIDYLAZO COMPOUNDS AS ANALYTICAL REAGENTS
A REVIEW

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ملخص

هناك عدد كبير من مشتقات ٢ ـ بيريديل أزو تستخدم ككواشف طيفية لتقدير عدد كبير من ايونات العناصر المختلفة وتتضمن هذه الورقة سرد الطرق المختلفة ، كذلك الظروف الملائمة لتقدير تلك العناصر باستخدام القياسات الطيفية .

- ABSTRACT -

A large number of 2–pyridylazo compounds have been proposed as reagents for the spectrophotometric determination of several metal ions.

The application of 2–pyridylazo compounds for the determination of many metal ions is listed and several procedures are described to illustrate the fundamental conditions for the spectrophotometric determination of these metal ions.

I NTRODUCTION

During the last thirty years , the analytical application of pyridylazo compounds has been studied extensively . Two representatives of this group , 1–(2–pyridylazo)–2– naphthol (PAN) and 4 – (2–pyridylazo) resorcinol (PAR) , have proved to be very versatile reagents for the analysis of several metals .

Although neither reagent is selective as chromogenic agent or as an extractant , new selective 2–pyridylazo derivatives have been proposed by several workers .

In search for new sensitive and selective reagents , a thorough study of some of the azo compounds containing halogen–substituted pyridine or naphthol has been made .

The aim of this review is to summarize the analytical aspects of the 2–pyridylazo compounds .

SPECTROPHOTOMETRIC APPLICATIONS

1 – (2) PYRIDYLAZO – 2 – NAPHTHOL (PAN) :

1 – (2–Pyridylazo)–2–naphthol (PAN) as one of the earliest reagents used for the spectrophotometric determination of several metals . It acts as a terdentate ligand complexing with metals through the hydroxyl oxygen , pyridine nitrogen , and one of the azo group nitrogen atom .

PAN recommended as a spectrophotometric reagent by Cheng and Bray[1] where it gives a reddish colored chelates with Zn (II) , Cu (II) and Cd (II) . Among the metal tested , EDTA prevents all metals from reacting with the PAN . Under acidic conditions , Indium forms a red chelate with PAN[2] The spectrophotometric determination of Mn (II), Fe (II) ,Ga (III) Hg (II) ,and Y(III) with PAN was reported by Shibata [3] . The colored complexes formed by rare earth metals and PAN has been investigated [4].Traces of rare earth metals can be determined in the presence of many foreign metals .

Extraction characteristics of Fe(II) Co (II) and Ni (II) chelates with PAN have been studied by puschel et al [5] .

PAN forms a 2:1 complex with Thallic ion [6], which has been extracted, from 0.1– 0.5 N solution of a strong acid, by 0.3 N– bis (2–ethylhexyl) hydrogen phosphate in heptane.

In an ammoniacal medium, Uranium (VI) froms a red–violet complex with PAN [8–10], Which is sparingly soluble in water and extractable into chloroform or 0-dichlorobenzene. The molar extinction coefficient is 2.3×10^{4} l.mole^{-1} cm^{-1} at $\lambda_{max} = 560$ nm. EDTA and KCN have been used to mask the interfering metals.

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Extraction of Zn (II) with PAN in benzene and methyl isobutyl Ketone, was studied by means of atomic absorption, and the method of determination of zinc, by atomic absorption in the two mediums were compared. The latter medium is suitable for the determination of zinc traces in concentrated solutions of alkali and alkali earth salts [11]. The influence of $NaClO_4$, Na_2SO_4, NaCl, KBr, KI and KCNS on the extraction step and the Spectrophotometric determintion of zinc and cadmium with PAN reagent has been investigated [12].

PAN has been used for the determination of nickel at the µg / l level in natural water [13]. With one liter of sample the detection limits are 0.077 µg / l for fresh water and 0.34 µg / l for sea water.

PAN was the first of the azo reagents which applied to the determination of rhodium ($\epsilon = 1.15 \times 10^{4}$ l.mole^{-1} cm^{-1} at 598 nm in chloroform) [14,15].

Rhodium was determined with PAN in the presence of the other metals such as platinum, gold, and silver.

There is a remarkable increase in the methods used for determination of cobalt which are based on pyridylazo compounds. Traces of cobalt in the presence of nickel and other metals have been determined after the extraction with PAN into Chloroform [5,16–18].

Abu Zuhri found that cerium (III) reacts at pH 10.2 with PANin40%ethanol to form a red complex which has an absorbance maximum at 545 nm[19]

Using PAN , a simple and senstive approach has been developed for the spectrophotometric determination of Lanthanum (III)[20] . The molar extinction coefficient of the La (III) – PAN complex in 50% ethanol in water and at pH 9,6 is 0.55 x 10^4 l. mol^{-1} cm^{-1} . In pure ethanol,the molar extinction coefficient is 8 .0 x 10^4 l.mol^{-1} cm^{-1}

Generally , PAN can be used as analytical reagent for the determination of Ag (I)[21], Ga (III)[3] , Al (III)[25,26] , Bi (III)[22], Sb (III)[23] Sn (IV)[24] ,Fe (II)[3,27]Mn (II)[28] , Zr (IV)[29] , Nb (III) [30] , Pd (II)[31,32], Sm (III)[33] , Ir (IV)[34] and Ti (IV)[34,35] .

SUBSTITUTED-PAN :

In search for new sensitive and selective reagents , a thorough study of some of the azo compounds containing halogen–substituted pyridine has been made .

The heterocyclic azo compound , 1–(5–bromo–2–pyridylazo) –2–naphthol (5–Br–B–PAN) , forms various colored metal chelates , which can be extracted with different organic solvents [36] . Chelates stability is greatly affected by pH . The molar extinction coefficient of 5–Br–B–PAN are usually considerably greater than those of the B–PAN chelates . A correct choice of pH, solvent and masking reagents allows 5–Br–B–PAN to be made reasonably selective .

The possibility of 1–(5–chloro–2–pyridylazo) –2–naphthol (5–CL–B–PAN) as an analytical reagent was described by Shibata et,al[37] . He concluded that the molar extinction coefficient are usually greater than those of the B–PAN Chelate . Although the bathochromic shifts produced on chelation are not greater than those with 5–Br–B–PAN .

Zinc (II) reacts with 5–CL–B–PAN in aqueous solution ; the complex can be extracted with various organic solvents at pH 8–11[38] . The molar extinction coefficient in the ether extract is 8.4 x 10^4 L . $mole^{-1}$ cm^{-1} at 564 nm .

AtpH 9–11, cadmium (II) reacts with 5–CL–B–PAN to form a complex , which can be extracted with chloroform [39] . Common anions and cations do not interfere . The molar extinction cofficient in chloroform is 6.6 x 10^4 L . $mole^{-1}$ cm^{-1} at 566 nm .
1–(5-methyl-2 pyridylazo) –2–naphthol ($5–CH_3–B$ –PAN) is used as a reagent for the determination of rare earth elements and Uranium [41],

4-(2-PYRIDYLAZO) RESORCINOL (PAR) :

4 –(2–pyridylazo) resorcinol (PAR) forms a red 1:1 complex with Cu (II) at pH 1.5 – 2.5 [42] . Addition of 3% H_2O_2 solution masks large amounts of rare earth , zirconium , hafnium , thorium , gallium and aluminium . Iron masked with fluoride ion .

Thallium reacts with PAR to give a red , water soluble 1:2 complex absorbing at 520 nm[43] . The complex is stable for 48 hoursupto 90 °C and the optimum pH value is 3.5 – 4.5.

Subrahmanyan and Eshwar [44] intoduced PAR as an analytical reagent and its reaction with hafnium . Hafnium forms an 1:1 orange–red chelate in the presence of ascorbic acid at 2.5 . A three fold amount of Zirconium may be present without interference There is interference by Fe (II) , Co (II) , Ni (II) , Ti (IV) , CN^- , EDTA , F , citrate, tartrate and oxalate .

The complexes formed by vanadium with PAR have been examined by Budevsky[45] . The methods were applied to determine vanadium in petroleum [46] , sea water [47] , and copper ores [48],

PAR reacts with lead ions in weakly ammoniacal medium to form a red complex ($\epsilon = 4.0 \times 10^4$ L. mole^{-1} cm^{-1} λmax = 520 nm) [49,50], which has been used to determine lead in steel , brass , and bronze[51] .

PAR forms two water soluble complexes with indium [52,53] . The 1:1 and 1:2 , (In : PAR) complexes are formed at approximately pH 3 and pH 6 respectively . . The PAR method for determining indium at pH 6 is sensitive but not selective . . At pH 3 , the selectivity of the method increases , but the sensitivity decreases .

Pollock[54] studied the reaction between PAR and Uranium . A 1:1 complex at pH 8 is formed and conforms to Beer's law up to 7 µg of U/ml .

Generally , PAR can be used as analytical reagent for Ag (I)[55] , Hg (II) [56] , Cd (II)[57] , Bi (III)[58] , Sb (III)[59] ,Sn(IV)[60] , Ga (III)[61] , Sc (III)[62] , Fe (II)[20] , Mn (II)[63,64] , Zn (II)[64–66] , Ti (IV)[67] , Zr (IV)[68] , Mo (VI)[69] , Nb (III)[70] , Au (III)[71] , Pd (II)[72,73] , Rh(III)[74] , Ru (III)[75] , Os (VIII)[76] , Th (IV)[77] , Eu (III)[78] , and Cr (III)[79] .

SOME OTHER PYRIDYLAZO COMPOUNDS AS ANALYTICAL REAGENTS :

4–(2–pyridylazo) –1 , 3–diaminobenzene (PADAB)and its – derivatives such as 5–Cl–PADAB , 5–Br–PADAB , 5–I–PADAB , 3,5–diBr–PADAB , and 3,5–diCl–PADAB were prepared . These compounds are used as chromogens for the spectrophotometric determination of traces of Co (II)[80] . These reagents show high color stabilities and extreme sensitivities in their reactions in strongly acidic medium . The effective molar extinction coefficient range between 1.0 and 1.23 x 10^5 1.mole^{-1}cm^{-1} , as shown in table 1.

Only iron and chromium interfere , the presence of flouride and hydroxylamine makes the reaction specific . 5–Br–PADAB has been applied to the determination of Co (II) in silicate rocks and meteorites with good precision and accuracy .

TABLE 1

Molar Extinction coefficient And Sensitivity For The Cobalt (II) Complexes :

Reagent	λmax (nm)	ϵx10^5(L.mole^{-1}cm^{-1})	μg/cm^3	ϵx10^5(L.mole^{-1}cm^{-1}) Shibata[81].
PADAB	565	1.00	0.00059	1.07
5–Cl–PADAB	570	1.13	0.00052	1.12
5–Br–PaDAB	575	1.16	0.00051	1.17
5–I–PADAB	580	1.18	0.00050	—
3,5–Cl–PADAB	585	1.19	0.00050	—
3,5–Br–PADAB	590	1.23	0.00048	—

Fifteen azo dyes contaning the m–dimethylaminophenol group were synthesized , and their analytical potential for the determination of Co (II) , Ni (II) , Cu (II and Zn (II) were studied spectrophotometrically[82] . Among these reagents , the heterocyclic azo derivatives are most suitable as chromogenic reagents. The best reagents are the 2–pyridylazo compounds .These complexes with Cu (II) , Zn (II) , and Ni (II) show molar extinction coefficient of the order of 10^5 . In these reagents , the para–substituted dimethylamino group next to the azo group seems to play an impotant role in achieving high molar absorptivity and stability of the metal complexes .

Florence and co–workers[83] introduced 2– (2– pyridylazo) –5–diethyl amino–phenol (PADAP) as an analytical reagent for U (VI) . This new reagent is almost twice as sensitive towards U (VI) as PAR with a molar extinction coefficient of 7.61×10^4 $l.mole^{-1}cm^{-1}$, at pH 8.2 and 564 nm . Generally , we can say that , the most sensitive reactions are provided by PADAP and its halogen derivatives , 5–Br–PADAP , 5–Cl–PADAP and 3,5–diBr– PADAP.

2–(5–chloro–2–pyridylazo)–5–diethylaminophenol (5–Cl– PADAP) has been used as a chromogenic reagent for Spectrophotometric determination of lead (II)[84] , Cobalt (II) [85,86] , gallium (III)[86], iron (III)[87] , Cadmium(II)[88] , and Zinc (II)[89].

. 2–(3,5–dibromo–2–pyridylazo) –5–diethylaminophenol (3,5–diBr–PADAP) can be used as an analytical reagent , and reacted with Sb (III)[90] , V (III)[91] , Ag (I)[92] and U (VI)[93] .

2– (5–bromo–2–pyridylazo) –5–diethylaminophenol (5–Br–PADAP) has recently attracted much attention as a spectrophotometric reagent because of its high sensitivity and good selectivity . This reagent has been used to determine many elements such as Cd (II)[94] , Sb (III)[95] , Co (II)[96] Ti (III)[97] Zn (III)[98] , U (VI)[99,100] , Hg (II)[101] , Cu (II)[102] , Ni (II)[103] and Mn (II)[104] . On the other hand , 5–Br–PADAP is a useful and sensitive reagent for La (III) , Ce (III) and Y (III)[105] . The pH of solution should be adjusted to 9.94 , 10.4 and 11.0 for the determination of Y (III) , Ce (III) and La (III) respectively . The stability of these complexes are in the order Y (III) >Ce (III) >La (III) . Thorium (IV) reacts with 5–Br–PADAP to form a reddish brown complex at pH 4.86[106] . Rare earth ions do not interfere because they form complexes with 5–Br–PADAP at higher pH's (>9.94) as mentioned above [105].

Miscellaneous reagents include 3–(2–pyridylazo) chromotropic acid for Cu (II)[107] ,Ni (II)[108] and Be (II)[109]. 1–(2–pyridylazo) phenanthrol for Cu (II)[110],U(VI)[111] and pt (IV) [112]. 4– (2–pyridylazo) –m–phenylenediamine and its 5–Chloro and 5–bromo derivatives for Co (II)[80,113]. 1– (5–bromo2pyridylazo)–5–ethylamino–p-Cresol and 3,5–dibromo derivative for Indium (III)[114]. 5–(2–pyridylazo)–p–cresol and 5– (2–pyridylazo)–2–monoethyl amino–p–cresol for Zn (II)[115].6– (2–pyridylazo) thymol for V(V)[116].6–(2–pyridylazo) 3,4–xylenol for Sn (IV)[24] .3– (2–pyridylazo) –2,6–diaminopyridine and its 5–chloro derivative for Co (II) [117,118] . 5– (2–pyridylazo)–2,4–diaminotoluene (PADAT) , 5–Me–PADAT , 3,5–diCl–PADAT and 3,5–diBr–PADAT for Co (II)[119] . 2–(3,5–dibromo–2–pyridylazo) –4–diethylaminobenzoic acid for Ni (II) , Cu (II) and Fe (II) [120] .

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