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Progress in and Prospects for the Use of Heterocyclic Azo-compounds in Analytical Chemistry

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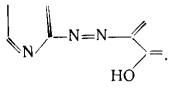
The effects of substituents in bases and coupling components on the properties of heterocyclic azo-compounds are examined in the pyridine, anabasine, thiazole, quinoline, and antipyrine series and their compounds with metal ions. Methods are indicated for varying the sensitivity of the reagents, the stability of the resulting complexes, and the selectivity of reactions with inorganic ions. Prospects for the use of heterocyclic azo-compounds in analytical chemistry are noted. A list of 199 references is included.

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I. INTRODUCTION

Heterocyclic azo-compounds include reagents containing the atomic grouping



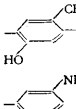
The bases used are amines of nitrogenous heterocycles (pyridine, thiazole, benzothiazole, quinoline, pyrimidine, anabasine, antipyrine, and other derivatives), and the coupling components are aromatic hydroxy-compounds (phenol, resorcinol, naphthol, quinolinol, etc.). The number of papers on heterocyclic azo-compounds and their analytical applications increases annually, having reached around 150, 400, 700, and above 1100 by 1964, 1968, 1972, and the end of 1975 respectively. Such compounds are widely used as reagents for photometric and extraction–photometric determinations, as complexometric indicators, and as indicators in the determination of various anions by precipitation[1-4]. They form with many metal ions intensely coloured compounds, the complexing reactions exhibiting high contrast, which underlies many methods for determining inorganic ions by their use.

Most of the publications have been devoted to the practical application of heterocyclic azo-compounds in the analysis of naturally and industrially occurring substances, and very few studies have been concerned with elucidating the reasons for the great reactivity of these reagents, examining the effect of substituents on the properties of reagents and complexes, and other theoretical aspects.

The present Review deals only with the optical characteristics of the complexes, since, as noted above, the ability to form coloured complexes with metal ions underlies methods for determining the latter. Table 1 lists structural formulae and the abbreviations for the reagents adopted in the literature.

The following symbols are used in the Review: ϵ is the molar extinction coefficient, β the overall stability constant of the complex, K_{eq} the equilibrium constant of complex formation, K_{OH} the dissociation constant of the hydroxy-group *ortho* to the azo-group, K_{NH} the dissociation constant of the protonated heterocyclic nitrogen atom *ortho* to the azo-group, E the dielectric constant of the solution, and μ the ionic strength of the solution.

Table 1. Structural formulae and abbreviations for heterocyclic azo-compounds.

Coupling component	Base: pyridine	thiazole	quinoline	methylanabasine	antipyrine
	1-PAN	1-TAN	1-(2-QAN)	1-MAN	1-ANAN
	2-PAN	2-TAN	2-(2-QAN)	2-MAN	2-ANAN
	*o*-PAC	*o*-TAC	–	–	–
	PAR	TAR	2-QAR	MAAR	ANAR
	PAAC	TAAC	2-QAAC	MAAC	ANAC
	–	–	–	MAAP I	–
	PAAP	TAAP	2-QAAP	MAAP II	ANAP

The value of photometric organic reagents is determined by the totality of properties of reagents and complexes—the sensitivity and selectivity of the reagent, the degree of contrast in the colour change of the solution on complex formation, the stability of the complexes formed—properties which will be surveyed below.

II. SENSITIVITY OF HETEROCYCLIC AZO-COMPOUNDS

The sensitivity of reagents in photometric analysis is expressed by the limiting dilution or the detectable minimum. Increasing use has been made during recent years of the molar extinction coefficient as the most objective characteristic of the sensitivity: from its value together with the sensitivity of the instrument, the minimum determinable optical density, the volume of the solution, and the thickness of the absorbing layer we can calculate the limiting dilution or the detectable minimum. The extinction coefficient ϵ is used in the present Review as a measure of the sensitivity of a reagent.

Role of Base

Azo-compounds derived from pyridine are usually the most sensitive. They are followed by anabasine, quinolin-2-amine, thiazole, and finally antipyrine derivatives. This rule is confirmed with reagents formed with resorcinol (Table 2), ethylamino-*p*-cresol, and *m*-diethylaminophenol, and is valid for the majority of ions. However, not only the nature of the heterocycle but also the position of the amino-group relative to the heterocyclic atom is significant. Reagents based on quinolin-2-amine are more sensitive than those based on quinoline-8-amine. Thus $10^{-4}\epsilon$ has the values 7.1 and 6.0 for the compounds of cobalt(II) with 2-QAAC and 8-QAAC respectively; the corresponding values for the gallium compounds are 9.8 and 7.4, and with 2- and 8-QAAT 10.5 and 7.7.[17,18] Derivatives of quinolin-2-amine are preferable to those of the 8-isomer also for copper and indium.

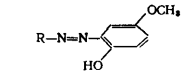
Table 2. Effect of base on sensitivity of determination of ions (resorcinol derivatives)*.

Reagent	$10^{-4}\epsilon$				
	Cu^{II}	Ga^{III}	In^{III}	Ni^{II}	Co^{II}
PAR	5.9[5]	9.9[6]	3.3[7]	7.3[8]	6.0[9]
TAR	3.1[10]	6.3[11]	2.3[12]	6.6[13]	5.6[9]
2-QAR	4.9[14]	4.7[14]	6.0[14]	5.5[14]	6.6[14]
MAAR	5.4[15]	—	3.8[16]	—	—

* Complexes having a dissociated *p*-hydroxy-group are compared.

The sensitivity of a reagent is little affected by increase in the number of heteroatoms in the base, provided that the latter does not contain fused rings. Indeed, reagents derived from pyridine and from thiazole are closely similar in sensitivity, although introduction of the new heteroatom (sulphur) may change the reactivity of the reagents and the mechanism of complex formation. The optical characteristics of the reagents change significantly. The introduction of fresh heteroatoms, e.g. nitrogen, has a substantial effect on the properties and the ionic form of the reagent, the absorption maxima and intensity, and the dissociation constants (Table 3). The properties of the complexes are also changed: for the copper compounds of TAMP, TRAMP, and TEAMP, for example, the light-absorption maxima occur respectively at 631, 578, and 578 nm, the logarithms of the stability constants are 9.8, 16.28, and 10.56, and the sensitivity ($10^{-4}\epsilon$) is practically the same (0.71 and 0.84 for the TRAMP and TEAMP compounds)[19].

Table 3. Effect of number of heterocyclic nitrogen atoms on properties of reagents[19] (2 vol.% ethanol).



Reagent (R)	Form	λ_{max}, nm	$10^{-4}\epsilon$	pK_n
TAMP 	H_3R^{2+}	523	1.4	—0.03±0.03
	H_2R^+	468	1.2	8.13±0.02
	R^-	561	1.4	
TRAMP 	H_3R^{2+}	470	0.6	—0.10±0.02
	H_2R^+	432	0.5	7.79±0.05
	HR	520—550	0.5	9.69±0.04
	R^-	494	1.1	
TEAMP 	H_3R^{2+}	468—480	1.4	—2.81±0.05
	H_2R^+	460	5.3	3.37±0.06
	HR	422	5.4	8.69±0.06
	R^-	503	9.2	

A similar rule is observed with the six-membered pyridine and pyrimidine heterocycles: thus the zinc(II), copper(II), and nickel(II) compounds of 2-pyrid-2′-ylazo-1-naphthol (1-PAN) have sensitivities ($10^{-4}\epsilon$) of respectively 2.5, 2.1, and 2.2,[20] while the corresponding 2-pyrimidin-2′-ylazo-1-naphthol (1-PAN) compounds have 2.5, 2.0, and 2.1.[21] The absorption maxima of the two series of complexes are slightly displaced (by 2–4 nm).

Hence the sensitivity of heterocyclic azo-compounds towards metal ions should be enhanced primarily not by changing the nature of the base but by a different procedure, e.g. by introducing substituents at certain positions. Monatomic substituents having a high Coulombic integral, e.g. chlorine or bromine, may have a significant influence on the sensitivity of reagents when located at position 5 in the pyridine ring[22–25]. Reagents containing bromine are usually more sensitive than those with chlorine at this position (Tables 4 and 5).

Table 4. Comparative sensitivity of 2-Pan and its halogenated derivatives.

Ион	2-PAN (Ref.26)		5′-Cl-PAN (Ref.26)		5′-Br-PAN (Ref.27)	
	λ_{max}, nm	$10^{-4}\epsilon$	λ_{max}, nm	$10^{-4}\epsilon$	λ_{max}, nm	$10^{-4}\epsilon$
Mn^{II}	562	4.8	566	7.2	574	7.2
Ni^{II}	570	5.0	580	7—8	582	8—9
Cu^{II}	564	4.4	567	5.8	572	5.2
Zn^{II}	550	5.6	569	7.1	570	6.7
Pd^{II}	678	1.9	670	0.8	695	1.8
Cd^{II}	555	4.9	560	7.0	568	7.3

The effect of a methyl group can be traced only on a few complexes. For example, the sensitivity of resorcinol reagents towards indium is enhanced by the introduction of methyl: values of $10^{-4}\epsilon$ for the compounds with PAR and 4′–6′-CH_3–PAR are respectively 3.3, 4.5, 3.9, and 4.3; the bromo-derivative is more sensitive (5.6 for 5′-Br-PAR)[7,14]. Towards copper(II), cobalt(II), nickel(II), zinc(II), and

uranium(VI) PAR is more sensitive than its analogues containing methyl in the pyridine ring[43]: the sensitivity towards these ions diminishes in the sequence PAR > 4′-CH_3-PAR > 5′-CH_3-PAR > 6′-CH_3-PAR. Methylation of the pyridine or thiazole ring is evidently undesirable, since in most cases it lowers the sensitivity of the reagents (Table 6). The enhancement of sensitivity towards indium can be explained by the formation of compounds having the proportions M : R = 1 : 3 in the case of the methylated derivatives, but 1 : 1 compounds when indium reacts with PAR. The diminished sensitivity in the case of 3′-CH_3-PAR was attributed[43] to steric hindrance due to rotation of the hydroxy-group in the coupling component to the *trans*-position relative to the 3-substituent in the base. If this is true, any 3-substituent in the base, especially a bulky substituent, should diminish the sensitivity of the reagent. This rule applies to most ions (Table 7). Dibromo-derivatives are almost always less sensitive than the monobromo-derivatives, although in several cases more sensitive than the unbrominated reagents.

Table 5. Effect of halogenation of base on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$					
	Co^{II}	Cu^{II}	Pd^{II}	Ga^{III}	In^{III}	Tl^{III}
2-PAN	3.0[28]	4.4[27]	1.4[27]	2.2[29]	1.9[7]	2.2[30]
5′-Br-PAN	4.1[31]	5.2[27]	1.8[27]	—	1.1[27]	—
PAAC	7.4[32]	3.8[33]	2.8[34]	11.9[35]	2.9[36]	5.5[37]
5′-Br-PAAC	7.5[32]	5.4[33]	4.0[34]	11.5[35]	5.0[38]	8.6[25]
PAAP	8.6[39]	3.8[24]	4.7[40]	9.6[41]	7.5[42]	6.6[25]
5′-Br-PAAP	9.8[39]	6.2[24]	4.3[40]	12.3[41]	7.8[42]	11.9[25]

Table 6. Effect of methylation of base on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$				
	Cu^{II}	Ni^{II}	Co^{II}	Ga^{III}	In^{III}
PAR	5.9[5]	7.1[44]	6.0[9]	9.9[6]	3.3[7]
6′-CH_3-PAR	4.7[14]	5.1[14]	5.4[14]	4.2[14]	4.3[14]
TAR	3.1[10]	6.6[13]	5.6[9]	6.3[11]	—
4′-CH_3-TAR	2.4[45]	—	3.8[46]	—	—
TAAC	3.7[45]	—	5.8[46]	6.5[47]	3.7[23]
4′-CH_3-TAAC	3.1[45]	—	—	—	2.5[23]

Table 7. Effect of bromination on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$								
	V^V	Co^{II}	Cu^{II}	Ga^{III}	Nb^V	Pd^{II}	In^{III}	Tl^{III}	Bi^{III}
PAR	3.6[48]	6.0[9]	5.9[5]	10.2[49]	3.5[50]	1.8[51]	3.3[7]	2.9[12]	1.1[5]
5′-Br-PAR	—	5.6[9]	—	—	2.1[52]	—	5.6[7]	—	—
3′,5′-Di-Br-PAR	—	2.4[9]	—	—	1.6[52]	—	—	—	—
PAAC	3.8[53]	7.4[32]	3.8[33]	11.9[35]	3.9[54]	2.8[34]	2.9[36]	5.1[37]	4.4[55]
5′-Br-PAAC	3.7[53]	7.5[32]	5.4[33]	11.5[35]	3.5[50]	4.0[34]	5.0[38]	8.6[25]	4.6[56]
3′,5′-Di-Br-PAAC	4.1[53]	6.0[32]	4.7[33]	10.4[35]	2.3[50]	3.5[43]	4.3[38]	5.2[37]	5.2[56]
PAAP	6.0[13]	8.6[39]	3.8[24]	9.6[57]	3.6[50]	4.7[40]	7.5[42]	6.6[58]	3.8[56]
5′-Br-PAAP	4.0[13]	9.8[39]	6.2[24]	12.3[41]	3.0[52]	4.3[40]	7.8[42]	11.9[25]	5.8[56]
3′,5′-Di-Br-PAAP	5.0[13]	9.3[39]	5.9[24]	8.8[41]	2.0[52]	4.1[40]	5.0[42]	9.2[25]	6.6[56]

A sulpho-group is usually introduced to increase the solubility of the reagent and of the complex. It has little effect on the sensitivity of the reagent or the degree of contrast of the reaction. For example, values of $10^{-4}\epsilon$ for compounds of palladium with TAR, TAR-5′-sulphonic acid, 2,4-dihydroxy-5-thiazol-2′-ylazobenzoic acid, and its 5′-sulpho-derivative are respectively 0.93, 0.93, 0.82, and 0.69.[59,60]

From the above effects of substituents it may be concluded that reagents based on 5-bromopyridin-2-amine should be the most sensitive.

Role of Coupling Component

It was shown[22,23] by a quantum-chemical method that substituents introduced *para* to the azo-group into the coupling component may change significantly the sensitivity of the reagents: the more polarisable the substituent, the more sensitive the reagent. The sensitivity should thus increase in the sequence of reagents containing the substituent

phenol < naphthol < resorcinol < ethylamino-*p*-cresol < diethylaminophenol

Naphthol derivatives are used most often, but the general rule is not observed with azonaphthols based on pyridine and anabasine. Among pyridylazonaphthols, for example, 1-PAN is more sensitive than is 2-PAN: the corresponding values of $10^{-4}\epsilon$ for the nickel(II) compounds are 2.2 and 1.9,[20] for cobalt(III) compounds 3.3 and 2.5,[27,31] cobalt(II) 3.9 and 3.0,[28,31] copper(II) 4.8 and 4.4,[27,61] zinc(II) 6.6 and 5.8,[62,63] and thallium(III) compounds 3.9 and 2.2.[30,63] With anabasine, 2-naphthol derivatives are the more sensitive: values of $10^{-4}\epsilon$ for the copper(II) compounds of 1-MAN and 2-MAN and respectively 2.2 and 3.0;[15] the corresponding values for the cobalt(II) compounds are 1.0 and 1.9.[65,66] The influence of the substitution in the coupling component on the sensitivity of the reagents is shown in Tables 8 and 9.

Table 8. Effect of coupling component on sensitivity of reagents.

Reagent	$10^{-4}\epsilon$				Reagent	$10^{-4}\epsilon$			
	V^V	Co^{II}	Nb^V	Cu^{II}		V^V	Co^{II}	Nb^V	Cu^{II}
o-PAC	0.7[53]	1.5[32]	0.6[52]	0.9[67]	PAAP	6.0[53]	8.6[39]	3.8[52]	3.8[24]
2-PAN	1.7[27]	3.0[28]	—	4.4[27]	TAR	2.7[68]	5.6[9]	3.2[69]	3.1[10]
PAR	3.6[48]	6.0[9]	3.5[50]	5.9[5]	TAAC	2.8[53]	5.8[46]	3.6[70]	—
PAAC	3.8[53]	7.4[32]	3.9[54]	3.8[33]	TAAP	3.5[71]	7.0[39]	3.5[70]	—

Table 9. Molar extinction coefficients of compounds of azo-derivatives of anabasine with metal ions.

Reagent	$10^{-4}\epsilon$				Reagent	$10^{-4}\epsilon$			
	Mn^{II}	Cu^{II}	Co^{II}	In^{III}		Mn^{II}	Cu^{II}	Co^{II}	In^{III}
1-MAN	3.8[72]	2.2[15]	0.8[73]	1.9[74]	MAAP I	7.6[72]	4.1[15]	—	—
MAAR	6.1[72]	5.4[15]	—	3.8[16]	MAAP II	11.2[72]	5.6[75]	7.8[75]	6.1[75]

Resorcinol derivatives, able to form two types of complexes, occupy a special position. In acid medium the *para*-hydroxyl does not dissociate, and *protonated* complexes (MRH) are formed. The degree of contrast in the change in colour on complex formation is very great, especially with complexes of cobalt(II) and the platinum metals; the

sensitivity of the reagents is close to that of azo-derivatives of phenol. In neutral medium the *para*-hydroxyl begins to dissociate, which is equivalent to introduction of an auxochrome into the reagent molecule. The complexes formed have been termed *normal* (MR), and are intensely coloured (Table 10); they are extracted only by polar solvents such as alcohols. The conversion of protonated into normal complexes is reversible and very rapid. The former may find application in analytical chemistry, despite the weakness of their colour. They are formed only by certain metal ions, and in acid medium, where interaction of these ions with heterocyclic azo-compounds is highly selective, the complexes are readily extracted by non-polar solvents. After selective extraction they can be re-extracted by a buffer solution as normal complexes having high molar extinction coefficients.

Table 10. Molar extinction coefficients of protonated and normal complexes (MRH and MR).

Reagent	Ion	$10^{-4}\epsilon$		Reagent	Ion	$10^{-4}\epsilon$	
		MRH	MR			MRH	MR
PAR	U^{VI}(Ref.76)	1.9	3.8	TAR	U^{VI}(Ref.81)	2.4	3.4
	Pd^{II}(Ref.77)	1.5	1.8		Pd^{II}(Ref.59)	0.9	2.2
	Rh^{III}(Ref.78)	0.9	2.7		Rh^{III}(Ref.82)	0.6	2.5
	Pt^{II}(Ref.79)	2.3	6.0		Cu^{II}(Ref.10)	1.9	3.1
	Pr^{III}(Ref.80)	1.1	2.0		Bi^{III}(Ref.10)	2.2	3.1
	Nd^{III}(Ref.80)	1.1	4.0		Pb^{II}(Ref.10)	2.0	3.0
	Er^{III}(Ref.80)	1.6	4.1		Zn^{II}(Ref.10)	3.1	3.5

The effect of dissociation of the *para*-hydroxyl on the sensitivity of reagents has been demonstrated convincingly. If this group is methylated, the sensitivity of the reagents is greatly decreased, although the degree of contrast of the reaction is not appreciably affected (Table 11).

Table 11. Molar extinction coefficients of compounds with thiazolylazoresorcinol and its methyl ethers.

Ion	$10^{-4}\epsilon$ for compounds with the reagent*		
	TAR	TAMR (Ref.83)	TAMG (Ref.83)
Cu^{II}	3.1 (505)[10]	3.1 (535)	1.3 (631)
Cd^{II}	3.2 (500)[10]	2.8 (508)	1.5 (598)
Hg^{II}	—	2.8 (537)	1.4 (628)
Zn^{II}	3.5 (500)[10]	2.7 (513)	1.6 (594)
Ni^{II}	6.6 (510)[13]	3.1 (520)	1.5 (608)
Co^{II}	5.6 (510)[9]	2.8 (511)	0.9 (618)
U^{VI}	3.4 (540)[81]	2.0 (530)[84]	1.4 (610)[84]

* Absorption maxima (nm) indicated in parentheses.

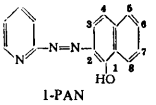
Both the coupling component and the base contain positions (e.g. 6) at which the sensitivity of the reagents is greatly diminished by substituents. Indeed, the reagent becomes much less sensitive, although the degree of constrast of the reactions changes just as greatly (Table 11). The marked decrease in sensitivity can be attributed to steric hindrance due to possible rotation of the *ortho*-hydroxyl to the *trans*-position with respect to the heterocyclic nitrogen atom. This also explains why *p*-cresol derivatives are the least sensitive reagents of all those listed in Table 8. The size of the substituent has different effects in azo-derivatives of pyridine and of thiazole, as is shown by Table 12 for compounds of uranium(VI) with PAR, TAR, and their derivatives[84].

Table 12.

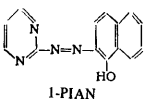
Reagent	PAR	6'-CH_3-PAR	6'-C_2H_5-PAR	6'-C_3H_7-PAR	TAR	6'-CH_3-TAP	6'-C_2H_5-TAR
$10^{-4}\epsilon$	3.8	3.6	1.3	1.7	3.2	3.0	2.9

The introduction of substituents into bases and coupling components at positions giving rise to steric hindrance on complex formation produces a sharp decrease in the molar extinction coefficient. For compounds of cobalt(II) with PAR, 5'-Br-PAR, 4-(3,5-dibromopyrid-2-ylazo)resorcinol, 2,6-dibromo-4-pyrid-2'-ylazoresorcinol, and 2,6-dibromo-4-(3,5-dibromopyrid-2-ylazo)resorcinol, for example, values of $10^{-4}\epsilon$ are respectively 6.0, 5.6, 2.4, 5.2, and 3.0.[9]

Table 13. Effect of sulphonation of naphthalene ring on properties of compounds of reagents with metal ions.



1-PAN



1-PIAN

Reagent	pK^*_{NH}	pK^*_{OH}	Zn^{II}		Cu^{II}		Ni^{II}		Pd^{II}	
			λ	$10^{-4}\epsilon$	λ	$10^{-4}\epsilon$	λ	$10^{-4}\epsilon$	λ	$10^{-4}\epsilon$
1-PAN (Ref.20)	2.29	10.00	545	2.5	566	2.1	548	2.2	—	—
1-PAN-4-SO_3H	2.03	8.63	528	2.6	555	2.3	563	4.2	650	1.2
1-PAN-5-SO_3H	2.39	9.11	543	2.3	567	2.3	580	4.1	631	0.9
1-PAN-6-SO_3H	2.48	9.13	545	2.5	570	2.2	582	4.3	675	0.9
1-PAN-7-SO_3H	2.46	9.09	543	2.6	569	2.2	579	4.2	670	1.0
1-PAN-8-SO_3H	2.85	10.44	589	2.7	582	2.2	592	4.3	703	1.3
1-PIAN (Ref.21)	0.92	9.66	543	2.5	564	2.0	544	2.1	—	—
1-PIAN-4-SO_3H	0.58	8.41	529	2.7	555	2.2	572	4.1	670	1.1
1-PIAN-5-SO_3H	0.87	8.87	541	2.7	565	2.2	583	3.9	690	1.0
1-PIAN-6-SO_3H	0.89	8.91	544	2.7	559	2.3	583	4.1	696	1.0
1-PIAN-7-SO_3H	0.87	8.66	542	2.7	567	2.2	585	3.9	693	1.0
1-PIAN-8-SO_3H	1.17	10.10	551	2.7	576	2.1	582	3.5	710	1.1

* μ = 0.1; 50 vol.% CH_3OH.

Sulphonation of the coupling component has hardly any effect on the sensitivity of the reagents, but influences the acid–base properties of the ligands (Table 13). Reactions showing the greatest and smallest contrast are obtained with a sulpho-group at positions 8 and 4 respectively. The sharp increase in sensitivity of the sulphonic acids towards nickel was attributed[20, 21] to the formation of compounds having Ni : R = 1 : 2, whereas 1-PAN and 1-PIAN yield 1 : 1 compounds. The interesting rule was established[20] that the bathochromic shift on passing from the protonated form H_2R^+ to the completely dissociated R^- is proportional to the overall

$$H_2R^+ \rightleftarrows 2H^+ + R^-$$

dissociation constant for 1-PAN, 2-PAN, and the sulphonated derivatives. This rule probably applies to other reagents, as the Reviewer has established for 1-PIAN and its sulphonic acids—data taken from Ref. 21 (Fig. 1 and Table 14).

Table 14. Absorption maxima and ionisation constants of PAN, PIAN, and their sulphonic acids.

Reagent	λ, nm		ν, cm^{-1}		Δν, cm^{-1}	pK_{NH}	pK_{OH}	$pK_{NH}+pK_{OH}$
	H_2R^+	R^-	H_2R^+	R^-				
2-PAN	425	495	23 530	20 200	3330	2.32	12.00	14.32
1-PAN	460	514	21 740	19 460	2280	2.29	10.00	12.29
1-PAN-4-SO_3H	465	498	21 510	20 080	1430	2.03	8.63	10.66
1-PAN-5-SO_3H	463	510	21 600	19 610	1990	2.39	9.11	11.50
1-PAN-6-SO_3H	465	513	21 510	19 490	2020	2.48	9.13	11.61
1-PAN-7-SO_3H	465	512	21 510	19 530	1980	2.46	9.09	11.54
1-PAN-8-SO_3H	468	532	21 370	18 800	2570	2.85	10.44	13 29
1-PIAN	455	523	21 980	19 120	2860	0.92	9.66	10.58
1-PIAN-4-SO_3H	445	508	22 470	19 690	2780	0.58	8.41	8.99
1-PIAN-5-SO_3H	447	523	22 370	19 120	3250	0.87	8.87	9.74
1-PIAN-6-SO_3H	452	527	22 120	18 980	3240	0.89	8.91	9.80
1-PIAN-7-SO_3H	449	523	22 270	19 120	3150	0.87	8.66	9.53
1-PIAN-8-SO_3H	448	531	22 320	18 830	3490	1.17	10.10	11.27

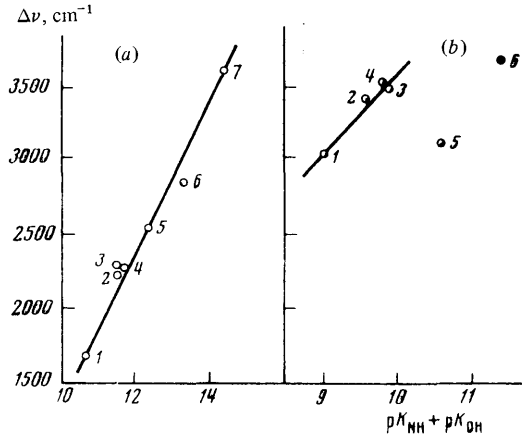


Figure 1. Effect of basicity of ligand on bathochromic shift in the reaction $RH_2^+ \rightleftharpoons R^- + 2H^+$ for: (*a*) pyridylazonaphthols[20]: *1*) 1-PAN-4-SO_3H; *2*) 1-PAN-5-SO_3H; *3*) 1-PAN-6-SO_3H; *4*) 1-PAN-7-SO_3H; *5*) 1-PAN; *6*) 1-PAN-8-SO_3H; *7*) 2-PAN; (*b*) pyrimidinylazonaphthols[21]: *1*) 1-PIAN-4-SO_3H; *2*) 1-PIAN-7-SO_3H; *3*) 1-PIAN-6-SO_3H; *4*) 1-PIAN-5-SO_3H; *5*) 1-PIAN; *6*) 1-PIAN-8-SO_3H.

Extraction enables the sensitivity of the reagent to be improved by concentrating the element. Little attention has hitherto been paid to the influence of the dielectric constant of the solution, which can be varied by suitable choice of solvent and the use of solvent mixtures. With aqueous–organic and organic-solvent solutions the molar extinction coefficients can also be changed. For example, among the solvents studied—tetrachloromethane, chloroform, benzene, diethyl and di-isopropyl ethers, and 4-methylpentan-2-one—the sensitivity for the determination of zinc[85] and cadmium[86] by means of 5′-Cl-2-PAN is greatest in diethyl-ether solution ($10^{-4}\epsilon$ = 8.5 and 6.6 for the respective metals) and least in di-isopropyl ether (5.1 and 5.4). The degree of contrast of the reactions remains almost unchanged (Table 15).

An advantage of heterocyclic azo-compounds is the great contrast of the change in colour of the solution on complex formation. This is responsible for their widespread use as complexometric indicators. Reactions with such compounds based on cresol derivatives and the reactions of almost all the reagents with cobalt(III) and the platinum metals exhibit especially high degrees of contrast: the absorption of light by the reagents at the absorption maximum of the complex is almost zero, while this maximum for the complex is displaced 200 nm or more relative to the absorption maximum of the reagents under the same conditions.

Table 15. Molar extinction coefficients of cobalt(II) compounds of heterocyclic azo-compounds in various solvents[31].

Solvent	Absorption max. (nm) (and molar extinction coefficients, $10^{-4}\epsilon$) of Co^{II} complexes of the reagents				
	2-PAN	Cl-PAN	Br-PAN	TAN	Br-TAN
CCl_4	2.7 (500)	2.4 (535)	3.1 (540)	3.2 (550)	4.8 (570)
$CHCl_3$	3.0 (525)	3.1 (535)	4.1 (540)	3.3 (555)	4.7 (570)
C_6H_6	3.5 (530)	2.7 (535)	4.0 (540)	3.4 (550)	5.3 (570)
$(C_2H_5)_2O$	3.2 (520)	— —	4.4 (540)	3.3 (550)	4.2 (560)
n-$C_5H_{11}OH$	2 7 (520)	2.9 (535)	4.6 (540)	3.3 (550)	— —

Table 16. Degrees of contrast of reactions of PAAC, PAAP, and their derivatives with metal ions.

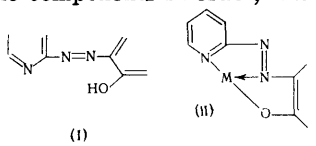
Reagent	Ga^{III} (Reg.17)		Cu^{II} (Ref.24)		Nb^{V} (Ref.52)	
	Δλ, nm	ϵ_c/ϵ_r	Δλ, nm	ϵ_c/ϵ_r	Δλ, nm	ϵ_c/ϵ_r
PAAC	100	91.0	105	2.7	145	41
5-Br-PAAC	110	100.0	105	14.9	145	31
3,5-Di-Br-PAAC	115	94.5	105	4.9	140	20
PAAP	110	46.0	100	5.9	145	38
5-Br-PAAP	125	137.0	115	6.4	140	27
3,5-Di-Br-PAAP	120	52.0	110	7.3	145	17

Improvement by monohalogenation of the analytical properties of the most promising reagents—PAAC and PAAP—increases the degree of contrast of complex formation as a consequence of a bathochromic shift; often the ratio of the molar extinction coefficients of complex and reagent ϵ_c/ϵ_r at the absorption maximum of the former becomes larger, the molar extinction coefficient of the compound with the monohalogenated reagent increasing considerably in comparison with the corresponding value of the unhalogenated reagent. Use of these reagents in photometric analysis is restricted by the poor sensitivity of azo-derivatives of *p*-cresol, despite the high degree of contrast of the reaction (Table 16).

III. STABILITY OF COMPLEX COMPOUNDS

Stability is an important characteristic of a complex compound, since the stability constants of the complexes and the acid dissociation constants of the ligands enable optimum conditions to be calculated for determining an inorganic ion and making its reaction with the chosen ligand as selective as possible. The stability of a complex compound depends on the denticity of the ligand, the basicity of the donor atoms in it, the acid–base properties of the

functional group involved in complex formation, the coordination number and the ionic radius of the central ion, the number and size of the rings formed, the molar proportions in which the components interact, and other factors.



(I) (II)

Most investigators regard heterocyclic azo-compounds as terdentate ligands. The atomic grouping (I) is involved in complex formation, and yields two rings (II) on interaction with one ligand. Of the two nitrogen atoms forming the azo-group that which is farther from the heteroatom of the base is the more reactive.

The multidenticity of heterocyclic azo-compounds as ligands explains that great stability of the complexes formed. Elimination of one of the atoms from the grouping (I) and its replacement by a carbon atom have marked effects on the stability of the complexes. For example, values of $\lg \beta_1$ for the compounds of copper with PAR, 2-PAN, 4-phenylazoresorcinol (replacement of heterocyclic nitrogen atom by a carbon atom), *o*-pyrid-2′-ylmethylenaminophenol (azo-group replaced by CH : N), *o*-pyrid-2′-yliminomethylphenol (azo-group replaced by N : CH), and *NN*-dimethyl-4-pyrid-2′-ylazoaniline (hydroxy-group eliminated from coupling component) are respectively 16.4, 16.0, 13.9, 13.8, 7.3, and 5.2.[2]

Basicity of Ligand

The basicity of the heterocycle decreases in the sequence of heterocyclic amines (values of pK_a given in parentheses) 2-aminoquinoline (7.34) > 2-aminopyridine (6.86) > 2-aminothiazole (5.39) > 2-aminobenzothiazole (4.51) > 8-aminoquinoline (3.99) > 2-aminopyrimidine (3.54).[87]

Table 17. Dissociation constants (pK_{OH}) of heterocyclic azo-compounds.

Reagent	Conditions	pK_{OH}	Ref.
4-Thiazol-2′-ylazoresorcinol	2 vol.% C_2H_5OH, $\mu = 0.1$	9.44	10
3-Thiazol-2′-ylazopyridine-2,6-diol	8 vol.% C_2H_5OH, $\mu = 0.1$	5.83	88
2-Quinol-2′-ylazo-1-naphthol	50 vol.% dioxan	10.65	89
7-Quinol-2′-ylazoquinolin-8-ol	$\mu = 0.1$	8.30	90
2-Benzothiazol-2′-ylazo-1-naphthol	isopentanol	7.90	91
7-Benzothiazol-2′-ylazoquinolin-8-ol	10 vol.% C_2H_5OH, $\mu = 0.01$	7.22	9[?92]
2-Pyrid-2′-ylazo-1-naphthol	20 vol.% C_2H_5OH, $\mu = 0.5$	11.11	61
7-Pyrid-2′-ylazoquinolin-8-ol	4 vol.% C_2H_5OH, $\mu = 0.4$	7.90	93

The introduction of a heterocyclic nitrogen or sulphur atom, having a lone pair of electrons not involved in the general chain of conjugation, is equivalent to introducing a strongly negative substituent such as a nitro-group. The acidic properties of such ligands should be intensified, and the stability of the resulting complexes diminished. If a heteroatom is introduced also into the coupling component, the acidity of the hydroxyl *ortho* to the azo-group is strengthened, and to a greater extent the closer is the heteroatom (resorcinol and pyridinediol, naphthalene and quinolinol azo-derivatives—Table 17).

Influence of Solvent

The widespread use of organic reagents in analytical chemistry poses the problem of studying the effect of solvents on the acid–base properties of ligands and the stability of complexes. If the reagent is present in protonated form (with the heteroatom protonated) in solution, its dissociation constant will increase with decrease in the dielectric constant of the solution; but if it is present in molecular or anionic form, it will become less acidic with decrease in the dielectric constant. This rule holds for 1-(2-QAN),[89] PAN and TAN,[94] PAR and TAR,[95] TAMR,[96] methyl 2-3′,4′-dihydroxyphenylazo-4-hydroxymethylthiazole-5-carboxylate[97], and 4-thiazole-2′-ylazocatechol[98]. For PAN and TAN, independently of the nature of the solvent (dioxan, ethanol, acetone, dimethylformamide) at concentrations of 20–50 vol.%, a single equation can be deduced[94] relating the conventional dissociation constant of the reagent with the dielectric constant of the solution (Table 18).

Table 18.

for PAN $pK_{NH} = 1.12 + 0.0175E - A\ (E = 35 - 75)$,
$pK_{OH} = 14.07 - 0.0260E - A\ (E = 50 - 75)$;
for TAN $pK_{NH} = 0.47 + 0.0235E - A\ (E = 45 - 70)$,
$pK_{OH} = 10.43 - 0.0215E - A\ (E = 50 - 70)$,

where $A = \dfrac{\sqrt{\mu}}{1 + \sqrt{\mu}}$ $(\mu = 0.1 - 0.5)$.

Table 19. Effect of dioxan on ionisation constants of 1(2-1-(2-QAN) and its copper and zinc complexes (μ = 0.1).[89]

Dioxan, vol.%	Reagent		Copper complex	Zinc complex	
	pK_{NH}	pK_{OH}	$\lg \beta_2$	$\lg \beta_1$	$\lg \beta_2$
30	2.65	10.03	12.74	—	—
34	2.59	10.16	12.85	—	—
40	2.33	10.35	13.04	—	—
44	—	—	13.20	9.73	—
50	2.03	10.65	13.35	9.88	20.25
54	—	—	—	9.97	20.34
60	—	—	—	10.13	20.29

This rule must be taken into account when the selectivity of determination is to be enhanced. With decrease in dielectric constant of the solution the ligand should interact with the test ion in a more acid medium because of the more acidic properties of the protonated heteroatom, while the complex should become more stable as a result of the increased basicity of the hydroxy-group (Table 19).

Molar Ratio of Components and Scheme of Complex Formation

The example of a single ligand, 2-PAN, can be used to show the variety of types of complexes formed with ions of different metals[99]: MR_2^0 with manganese, cadmium, nickel, and uranium(VI); MR_3^+ with iron(III), yttrium, indium, and cobalt(III); MR^{2+} with gallium and thallium(III); MR^0 with vanadium(V); and MR^+ with palladium(II) and copper(II). Complexes having M : R = 1 : 2 are in all cases more stable than the 1 : 1 complexes: for zinc(II) $\lg\beta_1 = 12.3$ and $\lg\beta_2 = 21.7$, nickel(II) 14.0 and 27.5, manganese(II) 8.5 and 16.4,[100] and copper(II) 16.2 and 30.5.[101] Highly coordinated complexes are especially stable: for example, $\lg\beta_{1-4}$ for the europium(III) complexes with 2-PAN have the values 12.4, 23.8, 34.5, and 43.7; the corresponding values for the holmium(III) complexes are 12.7, 24.4, 34.8, and 44.1; and for the complexes of ytterbium(III) with 2-TAN 9.8, 19.3, 28.5, and 37.4.[101,102]

Table 20.

$H_2R^+ + Pt(II) \rightleftarrows PtRH + 2H^+$	PAR	pH 1.6—2.1
$PtRH \rightleftarrows PtR + H^+$	PAR	pH 3.9—4.5
$HR + Pt(II) \rightleftarrows PtR + H^+$	PAN	pH 0.5—3.1
$H_2R^+ \rightleftarrows HR + H^+$	5-Br-PAAP	pH 2.0—3.2
$H_2R^+ + Pt(II) \rightleftarrows PtR + 2H^+$	PAAC	pH 0.5—2.0
	PAAP	pH 0.2—1.6
	5-Br-PAAP	pH —0.1—1.2

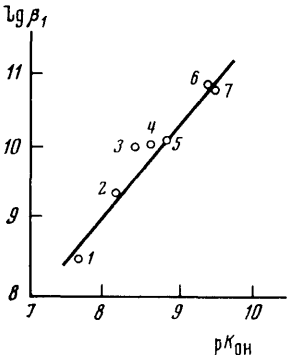


Figure 2. Effect of basicity of ligand[104] on stability of copper compounds[105] (1 : 1 complexes; spectrophotometric determination in presence of 20 vol.% of dioxan) of: 1) 4-chloro-2-thiazol-2′-ylazophenol; 2) 4-methyl-2-4′-methylthiazol-2′-ylazophenol; 3) 4-methoxy-2-thiazol-2′-ylazophenol; 4) 4-methoxy-2-4′-methylthiazol-2′-ylazophenol; 5) 4-methyl-2-thiazol-2′-ylazophenol; 6) 2,4-dimethyl-6-4′-methylthiazol-2′-ylazophenol; 7) 2,4-dimethyl-6-thiazol-2′-ylazophenol.

The diversity of the schemes of complex formation with azo-compounds of the pyridine series can be shown with platinum(II) as example (Table 20—charges on complexes omitted)[103]. These differences even in schemes involving related ligands must be considered in establishing the dependence of the stability of the complexes on the basicity of the ligand. Here we can examine a few cases of interaction and the corresponding types of correlation.

1. One complexing metal ion reacts with different related ligands by a single scheme of complex formation. In this case $\lg\beta$ can be plotted against $\lg K_{eq}$ and against pK_{OH} (Figs. 2 and 3). Departures from these relations often indicate incorrect determination of K_{eq} or pK_{OH}.

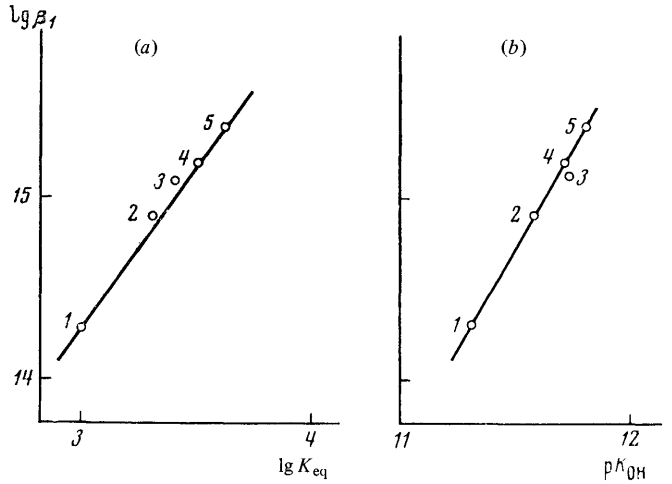


Figure 3. Effects of (*a*) complex-formation equilibrium constant and (*b*) basicity of ligand on stability of copper compounds of: *1*) 5-Cl-PAAC; *2*) 5-Br-PAAC; *3*) 5-Cl-PAAP; *4*) 1-PAN; *5*) 5-Cl-PAAP.[24]

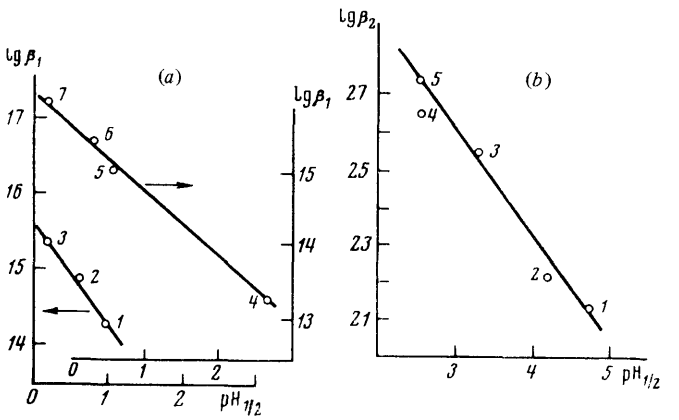


Figure 4. Effects of half-reaction pH on stability of: (*a*) copper compounds (1 : 1 complexes)[24] of: *1*) 5-Cl-PAAC; *2*) 5-Br-PAAC; *3*) 3,5-di-Br-PAAC; *4*) PAAP; *5*) 5-Cl-PAAP; *6*) 5-Br-PAAP; *7*) 3,5-di-Br-PAAP; (*b*) cobalt compounds (1 : 2 complexes)[9] of: *1*) PAR; *2*) 5-Br-PAR; *3*) 3,5-di-Br-PAR; *4*) tetrabromo-PAR; *5*) 2,6-dibromo-4-pyridylazoresorcinol.

A more universal relation is the dependence of $\lg\beta$ on $pH_{\frac{1}{2}}$:

$$-n\,pH_{1/2} = \lg K_p + n\lg C_R;$$

$$-n\,pH_{1/2} = \lg\beta - n\,pK_{OH} + n\lg C_R\ .$$

These results are plotted in Fig. 4 (for Cu:R = 1:1 and Co:R = 1:2) and were obtained on the assumption that the reagent concentration was 10^{-4}M. We can use these relations to estimate β from the experimental value of $pH_{\frac{1}{2}}$ (by plotting the pH dependence of the optical density).

2. Several complexing metal ions react with a single ligand according to the same scheme. Here it is advisable to plot $\lg\beta$ against $pH_{\frac{1}{2}}$ as in Figs. 4 and 5. For example, PAR is able to interact with metal ions according to several schemes, to form protonated and normal complexes (MRH and MR). For each scheme $pH_{\frac{1}{2}}$ is calculated by means of the appropriate equation:

$$M + H_2R \rightleftarrows MRH + H^+,$$

$$-pH_{1/2} = \lg\beta - pK_{OH} + n\lg C_R;$$

$$M + H_2R \rightleftarrows MR + 2H^+ \quad \text{or} \quad MRH \rightleftarrows MR + H^+,$$

$$-pH_{1/2} = \lg\beta - p\,K_{OH} - pK_{p\text{-}OH} + n\lg C_R$$

where $pK_{p\text{-}OH}$ is the logarithm of the reciprocal of the dissociation constant of the hydroxy-group *para* to the azo-group.

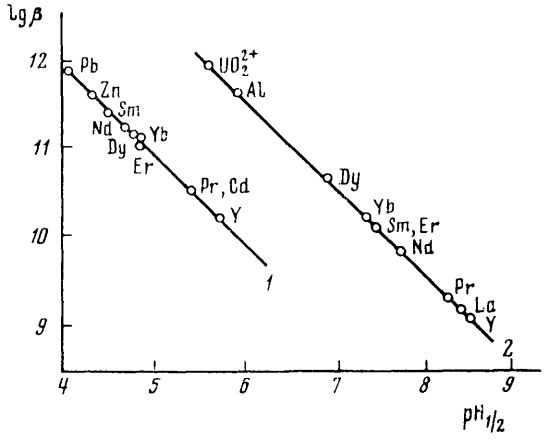


Figure 5. Stability sequences of PAR complexes: *1*) protonated (MRH); *2*) normal (MR). Constants for the rare-earth metal complexes taken from Ref. 80; that for uranium from Ref. 76; and those for lead, zinc, and cadmium from Ref. 17.

These relations enable us (*a*) to compare the stability of protonated and normal complexes of the same complexing agent, (*b*) to find $\lg\beta$ from the experimental value of $pH_{\frac{1}{2}}$, (*c*) to construct a stability sequence of complexes of different complexing metals with the same ligand, and (*d*) to confirm a suggested scheme of complex formation by means of the values found for $pH_{\frac{1}{2}}$ and $\lg\beta$.

3. One complexing metal ion reacts with related ligands according to different schemes. No correlation of the above types is possible here: only the dependence of $\lg\beta$ on $\lg K_{eq}$ is applicable (Fig. 6). Exceptions are the normal complex with PAR of type MR formed at pH 3.9–4.5 and the complex with 5-Br-PAAP formed at pH 0.1–1.2 (protonated complex of type MRH). It is easy to explain these exceptions: investigation of complex formation between platinum(II) and PAR established[79] the effect of the acetate ion on the conditions of complex formation and on the properties of the complex, in particular the molar extinction coefficient ($10^{-4}\epsilon$ = 6.0). This suggests the formation of the mixed-ligand three-component compound platinum–acetate–PAR. All azo-derivatives of pyridine other than 5-Br-PAAP (at pH 0.1–1.2) react with platinum in weakly acid medium; the acidity ranges roughly coincide, which may indicate indirectly that the ionic state of the platinum is the same. The complex formed with 5-Br-PAAP in strongly acid medium probably contains platinum in a different ionic state from that occurring on interaction with other azo-derivatives of pyridine. Therefore the properties of the resulting complex differ markedly from those of complexes formed in weakly acid medium.

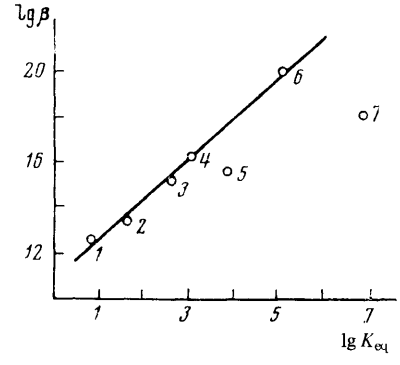


Figure 6. Effect of complex-formation equilibrium constants on stability of compounds of platinum(II) with pyridylazo-compounds[103]: *1*) 2-PAN; *2*) 5-Br-PAAP (ph < 2.0); *3*) PAAP; *4*) PAAC; *5*) PAR (ph < 4.5); *6*) PAR-(pH < 1.6); *7*) 5-Br-PAAP (pH ≃ 0).

Hence the scheme of complex formation can be confirmed by plotting $\lg\beta$ against $\lg K_{eq}$.

4. Complexing metal ions adjacent in the Periodic System react with related ligands. If complex formation is described by a single scheme, correlations are present between the stability of complexes of two complexing metal ions as well as between the stabilities of complexes of two neighbouring metals in a series, and the basicity of the ligand (Figs. 7 and 8). Departure from the correlation usually indicates an incorrect value of the dissociation constant of the reagent for the actual conditions: it is necessary to compare constants determined by the same method.

Very large differences exist between the values given by different authors for the stability constants of the same complex, e.g. $\lg\beta$ = 9.8,[107] 17.93,[12] and 24.17[108] for compounds of PAR with thallium(III), and 10.0[107] and 14.5[6] for the gallium compounds. These differences are partly

due to incorrect determination of the ratio of the components in the complex, the choice of scheme for complex formation, and the use of thermodynamic instead of conventional dissociation constants of the reagents, without taking into account the nature of the solvent and the dielectric constant of the medium.

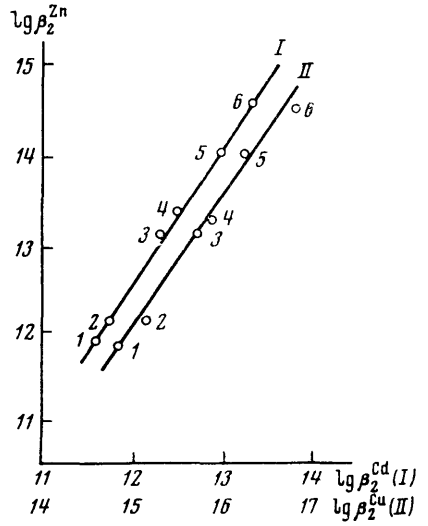


Figure 7. Relative stability constants (determined potentiometrically in 50% dioxan) of zinc, copper, and cadmium complexes[106] of compounds having the same type of ligands: *1*) 4-methyl-2-thiazol-2′-ylazophenol; *2*) 4-methoxy-2-thiazol-2′-ylazophenol; *3*) 2,4-dimethyl-6-thiazol-2′-ylazophenol; *4*) 4-methyl-2-(4,5,6,7-tetrahydrobenzothiazol-2-ylazo)phenol; *5*) 4-methoxy-2-4′-methylthiazol-2′-ylazophenol; *6*) 4-methoxy-2-(4,5,6,7-tetrahydrobenzothiazol-2-ylazo)phenol.

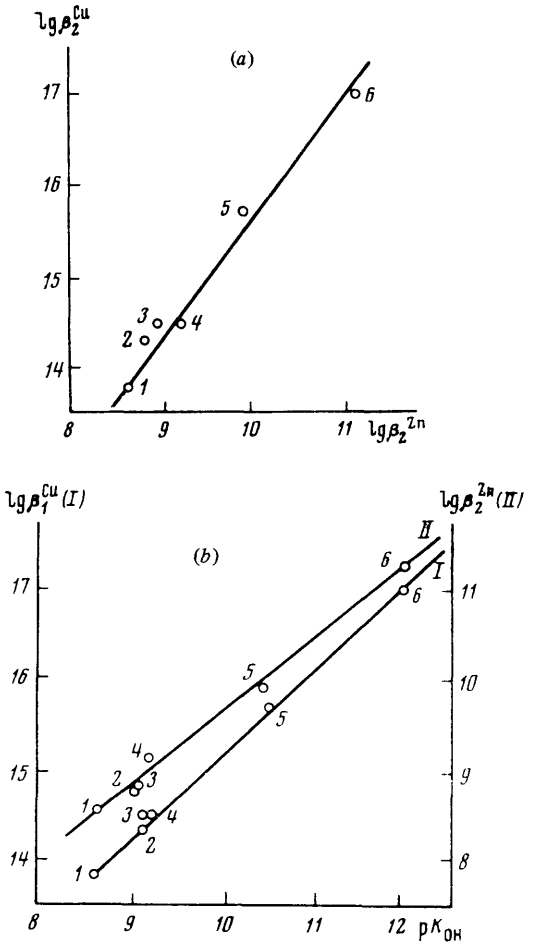


Figure 8. (*a*) Correlation of stability constants and (*b*) effect of basicity of ligands on stability of copper and zinc compounds$_2^{20}$ of: *1*) 1-PAN; *2*) 1-PAN-5-SO_3H; *3*) 1-PAN-7-SO_3H; *4*) 1-PAN-6-SO_3H; *5*) 1-PAN-8-SO_3H; *6*) 2-PAN.

Table 21. Methods of enhancing selectivity of reactions of heterocyclic azo-compounds with metal ions.

Method	Metals
Determination in acid medium	Cu^{109}, In^{110}, V^{111}, $Sb^{112,113}$, Pd^{114}
Difference in rates of formation	Co, $Cr^{44,115,116}$, Pd, Rh^{117}, Pt^{118}
Use of masking	Cu^{64}, Zn, Cd^{119}, Ga^{120}, In^{110}, Gd^{121} lanthanide [122] $U^{123,124}$
Coprecipitation of test elements	$Co^{9,125}$
Electrodeposition of interfering elements	Sm^{126}, Ti, Nb^{127}, V^{128}
Extraction of test ion	Cu^{129}, Zn^{62}, Ga^{130}, In^{110}, Nb^{131}
Extraction of interfering elements	Zn^{132}, Nb^{133}, U^{124}, $Mn^{134,135}$, Ni^{136}
Re-extraction of test or interfering elements	Zr^{137}, Sn^{138}, V^{139}, Nb^{140}, Co, Ni^{141}
Chromatographic separation	Mn^{142}, $Co^{143,144}$, Ni^{145}
Difference in absorption spectra	Fe[146], Ru, Os^{147}, Rh, Ir^{148}

IV. SELECTIVITY OF HETEROCYCLIC AZO-COMPOUNDS

Heterocyclic azo-compounds are very widely used for the photometric and the extraction-photometric determination of ions of almost all metals, other than alkali and alkaline-earth metals, in naturally occurring and artificially produced materials. This is promoted by the high sensitivity of the reagents and the selectivity of their reaction with a series of ions. Several methods are available for enhancing the selectivity of reactions with organic ligands, some of which have been achieved with heterocyclic azo-compounds (Table 21).

The wide range of ions with which heterocyclic azo-compounds react and the possibility of the extraction of complexes combined with spectral analysis have permitted the determinations e.g. of copper, cobalt, cadmium, gallium, iron, indium, manganese, nickel, thallium, and vanadium in alkali-metal bromates and iodates (at concentrations of $7 \times (10^{-7}-10^{-5})$ mass %).[149] After being concentrated by extraction, many elements can probably be determined in a single aliquot by atomic absorption or polarographic methods. The specificity of heterocyclic azo-compounds can usefully be exploited in activation analysis.

V. PROSPECTS FOR STUDY AND USE IN ANALYTICAL CHEMISTRY

Extraction

This procedure may prove very useful for enhancing sensitivity, improving the selectivity of determination, and the study of complex formation. Although reagents are often employed for extraction-photometric determination, the extraction of complexes of heterocyclic azo-compounds has not been adequately characterised. Several studies have recently been published on rates of extraction[150–152] and on the effect of various solvents on the distribution of reagents between organic and aqueous phases[101,151,152]. The rules thus found can be used to raise the selectivity of reagents.

Mixed-ligand Compounds

The introduction of two ligands into the coordination sphere of a complex will often improve the sensitivity and the selectivity of reagents. Mixed-ligand (mixed) complexes of heterocyclic azo-compounds are beginning to be investigated intensively. Some examples of mixed complexes are listed in Table 22.

Table 22. Mixed-ligand complexes of heterocyclic azo-compounds.

Complexing metal	Heterocyclic azo-cpd..	Second ligand
Al^{III}	PAR	antipyrine[154]
Ga^{III}	PAR	antipyrine[155]
In^{III}	PAR	antipyrine[154]
	PAN	acetate, chloride[152]
Ti^{IV}	PAR	H_2O_2[156], SCN[157], acetate[158], catechol[159], salicylic and 5-sulphosalicylic acids[160]
	PAN	H_2O_2[161]
V^{V}	PAR	H_2O_2[111,162], tetraphenylarsonium, tetraphenylphosphonium[163], diantipyrylmethane[164], quinine[165]
Nb^{V}	PAR	H_2O_2[166], oxalate, tartrate[50,52]
	PAN	H_2O_2[161]
Ta^{V}	PAR, PAN	H_2O_2[161,166]
Mo^{VI}	PAR,TAR	hydroxylamine[167,168]
Fe^{II}	PAR	hydroxylamine[169]
Co^{III}	PAR	quaternary ammonium bases[169]

Preparation of New Reagents

Besides the above heterocylic amines, derivatives of pyrrole[170], imidazole[171], antipyrine[172], triazole[19], tetrazole[173,174], and thiadiazole[175] have been used as bases, and bisazo-compounds have been prepared[173,174,176–178]. However, azo-derivatives of pyridine have hitherto been the most promising. The synthesis has begun of compounds containing as coupling components reagents that are themselves widely used in analytical chemistry, e.g. azo-derivatives of rhodanine[179–184], catechol[92,97,185–187], and chromotropic acid. The reagents possess several advantages in comparison with these compounds: stepwise complex formation is absent, the stability of the complexes is increased, and maximum absorption by the complexes takes place at longer wavelengths. This method is evidently most useful in the synthesis of new reagents.

Research Methods

Extraction has begun to be used as well as the widely employed photometric and potentiometric methods. The characteristics of the complex compounds are obtained by computer methods according to suggested programmes[96,171,188–190]; the advantages of such methods have been demonstrated many times. The structures of complex compounds and reactive forms of reagents are established by quantum-chemical calculations[22,23,191,192], nuclear magnetic resonance[193], determination of magnetic and dipole moments of the complexes[194,195], and by study of the infrared spectra[50,52,193,196–199].

* *
*

Heterocyclic azo-compounds are widely used as reagents for the photometric determination of elements and as complexometric indicators. The most sensitive are azo-derivatives of pyridine and 2-aminoquinoline, which form stable compounds with metal ions. A hydroxy-, amino-, or dialkylamino-group can usefully be introduced into the coupling component *para* to the azo-group to improve the properties of the reagents. A halogen—chloro or bromo—must be substituted *para* to the azo-group in the pyridine base. Promising complexometric indicators are thiazolylazo-compounds, which form intensely coloured and moderately stable compounds with metal ions. The solubility of these reagents can be increased by sulphonating the coupling component and the base. Reagents containing heterocyclic nitrogen in the coupling component—quinolinol, 2,6-dihydroxypyridine, etc. — should be valuable for the determination of readily hydrolysed ions of multivalent metals. Promising uses of extraction are the investigation of complex formation and the concentration of groups with the aim of subsequent polarographic, spectral, or atomic-absorption determination.

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