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SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF BINARY MIXTURES OF NICKEL, COBALT AND VANADIUM WITH 3-(PICOLYDENE)BENZENESULPHONIC ACID 2-HYDROXYBENZOYLHYDRAZONE

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SUMMARY

The synthesis and characterization of a water-soluble reagent, 3-(picolydene)benzenesulphonic acid 2-hydroxybenzoylhydrazone, is described. The reagent is stable in aqueous media. The colour reactions with nickel(II), cobalt(III) and vanadium(V) ions in slightly acidic solutions have molar absorptivities in the range 1.4–3.6 × 10^4 l mol^{-1} cm^{-1}. Simultaneous determinations of Ni, Co and V in binary mixtures are possible. Interference data are reported.

Aroylhydrazones can be regarded as carbonyl azomethines characterized by the grouping C=N—NH—CO—; they are easily prepared from the aroylhydrazide and a carbonyl derivative dissolved in a suitable solvent. Such compounds may possess tuberculostatic activity [1], attributed to the formation of stable chelates with transition metals present in the cell. The functional grouping causes these reagents to behave as bidentate ligands for metal ions, a five-membered ring being formed; coordination occurs by bonding from the first two nitrogen atoms and from the oxygen atom. Because of keto-enol tautomerism, coordination may occur through the oxygen of the keto form [2] or, more probably, of the enol form [3–9]. Chelates involving the azine grouping tend to give stable strongly coloured metal complexes [10, 11], whereas a pyridinic nitrogen in the carbonyl derivative improves the solubility and stability of aroylhydrazones. A common drawback of most of these reagents is their poor solubility in water.

Aroylhydrazones have been applied in the detection, determination and isolation of compounds containing the carbonyl group [1]. They have also been used in the detection and determination of various metals. Isonicotinoylhydrazones have probably been most studied but salicyloylhydrazones have been proposed for the determination of zinc or nickel [12], vanadium [13], iron [14] and some other metals [15].

In the present paper, the synthesis and properties of 3-(picolydene)benzenesulphonic acid 2-hydroxybenzoylhydrazone (PBSHB) are described.

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Optimum conditions for the separate spectrophotometric determination of nickel, cobalt or vanadium are reported, as well as for simultaneous determinations of binary mixtures of these metal ions.

EXPERIMENTAL

Reagents and equipment

Synthesis of PBSHB. First, 3-(picolinoyl)benzenesulphonic acid (PBS) was prepared as described by Bradsher et al. [16]. The product was recrystallized from 1:1 ethanol/water. To synthesize PBSHB, ethanolic solutions of PBS (1 g in 50 ml) and salicyloylhydrazide (0.64 g in 10 ml) were mixed and a few drops of concentrated hydrochloric acid were added. The precipitate was filtered off and crystallized from 3:2 ethanol/water. The results of analysis for C, H, N and sulphur were in good agreement with the empirical formula $C_{19}H_{15}N_3SO_5 \cdot 2H_2O$.

Solutions. The PBSHB is moderately soluble (1 g l^{-1}) in most common organic solvents, but is more soluble (>10 g l^{-1}) in dimethylformamide or water. Reagent solutions (0.1 and 1% w/v) in dimethylformamide or water were prepared by dissolving appropriate amounts of PBSHB dried at 110°C; aqueous solutions were prepared in dilute sodium hydroxide and then neutralized.

Standard solutions of nickel(II) (2.090 g l^{-1}) and cobalt(II) (2.054 g l^{-1}) were prepared by dissolving the pure metal in nitric and hydrochloric acid, respectively, neutralizing, and standardizing with EDTA (murexide and xylenol orange, respectively) in the usual manner. The vanadium(V) solution was prepared from sodium vanadate; it was standardized gravimetrically with silver nitrate.

Buffer solutions (chloroacetate for pH 3.7, acetate for pH 4.7, ammonia for pH 9.3, and borate for pH 9.2) and solutions of cations and anions of different concentration were prepared with distilled water from analytical-grade chemicals.

Equipment. Pye-Unicam SP8-200 and Perkin-Elmer Coleman 575 spectrophotometers were used with 1-cm glass or quartz cells. A Pye-Unicam SP3-300 infrared spectrophotometer (KBr discs) and a Metrohm Herisau E-516 Titriskop pH meter were also used.

Procedures

Acidity constants. To determine pK_{a2} and pK_{a3}, enough reagent solution was added to 10-ml volumetric flasks to give a final concentration of 2.52×10^{-5} M. The pH was adjusted with dilute hydrochloric acid or sodium hydroxide solutions and the absorbances were measured at 295, 305, 330 and 360 nm against an appropriate blank. The sulphonic acid group was examined similarly in solutions containing varying amounts of 70% (d = 1.67 g ml^{-1}) perchloric acid.

Spectrophotometric determination of nickel, cobalt or vanadium. To a solution containing up to 20 μg of Ni(II) or Co(II) or up to 50 μg of V(V), were added 1 ml of aqueous 0.1% (w/v) PBSHB solution, 0.5 ml of 1% hydrogen peroxide in the case of cobalt, and 4 ml of 0.5 M acetate buffer (Ni, Co or V) or 2 ml of 0.3 M chloroacetate buffer (V). The solution was diluted to the mark in 10-ml volumetric flasks. The absorbance was measured at 375 and 385 nm for nickel, 400 and 415 nm for cobalt and 395 nm for vanadium, against the appropriate blank solution.

Simultaneous determination of binary mixtures. To solutions containing up to 20 μg of Ni and Co, Ni and V, or Co and V, 1 ml of 0.1% (w/v) reagent solution, 5 ml of acetate buffer, and 0.5 ml of 1% hydrogen peroxide for mixtures of Co and Ni were added and the solution was diluted to the mark in 10-ml volumetric flasks. Absorbances were measured at 370 and 415 nm (Ni + Co), 370 and 420 nm (Ni + V), or 395 and 415 nm, 2 h after preparation of the sample for Co + V mixtures, against the appropriate blanks in all cases. The concentration of each ion in the mixture was calculated by solving simultaneous equations.

RESULTS AND DISCUSSION

Infrared spectra and thermogravimetric analysis of the reagent

The infrared spectrum of PBSHB was recorded between 200 and 4000 cm^{-1}. Comparison with the spectra obtained from the parent compounds and with the spectral data given by Domiano et al. [3] and Pelizzi et al. [8, 9] for related aroylhydrazones permitted assignment of the vibrational characteristics (Table 1).

The PBS spectrum shows two intense absorption bands in the 1150—1250 cm^{-1} region that can be attributed to symmetrical and antisymmetrical stretching of the SO_2 group (cf. [17—19]). Similar bands (1170—1235 cm^{-1}) are observed in the PBSHB spectrum. For both PBS and PBSHB, the strong band located at 3500—3400 cm^{-1} caused by OH stretching is noteworthy. The phenolic hydroxyl of the reagent is strongly associated (band at 2800—2550 cm^{-1}); this band disappears from the spectrum of PBS heated at 200°C, but is still observed for PBSHB heated at 200° C. Thermogravimetric analysis of PBSHB showed a constant weight between 100 and 200° C; a weight loss corresponding to two water molecules was observed between 200 and 250° C, indicating the presence of chemically bonded water molecules in PBSHB.

Ultraviolet-visible spectra of the reagent and dissociation constants

The spectral characteristics of PBSHB (2.52×10^{-5} M) were studied by recording its u.v.-visible spectra in several solvents (Fig. 1). It can be seen that the absorption maximum is shifted to higher wavelengths as the solvent polarity decreases, although polar solvents usually cause bathochromic shifts when $n \rightarrow \pi^*$ transitions are involved [3]. In aqueous solutions (Fig. 2), the maximum is around 325 nm in acidic solution (pH 2.6), whereas in alkaline media a new band appears at 365 nm. The corresponding pK_a values associated with these absorbing species, calculated by the Stenström-Goldsmith

TABLE 1

Infrared spectra of 2-benzoylpyridine (BP) and salicyloylhydrazide (SH) and their derivatives

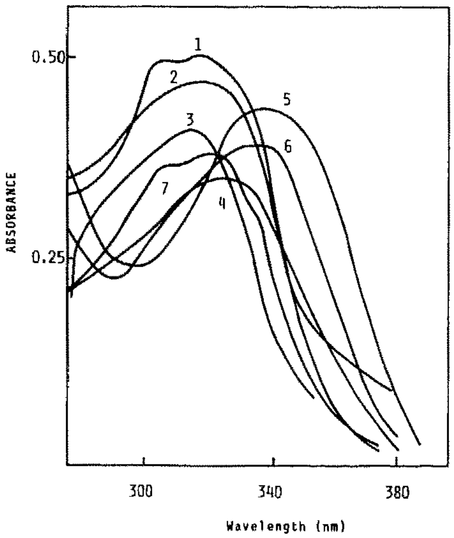
Assignment	BP	PBS	SH	PBSHB
ν_{OH} (water)		3410		3490
ν_{NH}			3320 s	
			3280 s	3260 w
			3140 w	
$\nu_{(=CH)}$	3080 w	3110 w	3060	3100
	3060 w	3090 w	3010	
	3010 w			
ν_{OH}		2900—2500 w	2850—2500	2800—2550 m
ν_{CO}	1670 vs	1660 s		
δ_{NH_2}			1640 sh	
Amide I			1625 s	1660 s
Aromatic ring	1600 w			1600 m
	1580 m	1585 s	1575 m	1570 w
Amide II			1560 s	1530 m
		1540 m	1510 m	1500 m
Aromatic ring	1460 w	1470 ms	1480 m	1460 m
	1440 ms		1440 m	
	1430 w	1430 m		
		1410 w		
ν_{SO_2}		1150—1250 vs		1235—1170 s
$\delta_{CH}{}^{a}$		820 m		810 w
	785 s	790 m	760 m	780 m
$\delta_{CH}{}^{b}$	750 s	755 vs		750 m
$\delta_{CH}{}^{a}$	700 vs	710 s		710 s
		700 vs		700 sh

[a] Out of plane (phenyl). [b] Out of plane (pyridine).

[20] and Sommer [21] methods, are pK_{a2} = 3.5 ± 0.2 (protonation of the pyridine N atom) and pK_{a3} = 6.7 ± 0.2 (deprotonation of the hydroxyl group). In perchloric acid media, the absorption band at 365 nm reappears. The pK_a corresponding to deprotonation of the sulphonic group, was found to be −1.81 ± 0.07, which was evaluated by the method of Yates and Wai [22], the absorbance being measured at 320 and 380 nm and the weight percentage of perchloric acid in the sample being converted to the equivalent Hammett acidity function.

Stability of the PBSHB solutions

The reagent is remarkably stable (>40 days) in ethanol, anhydrous acetic acid, chloroform and isoamyl alcohol, but less stable (about 15 days) in dimethylformamide. In aqueous buffered solution, the stability depends on pH: 15 days at pH 2.6, 20 days at pH 4.7 and >30 days at pH 9.3. In strongly acidic solution (2 M), the reagent is stable for only about 2 h, being decom-



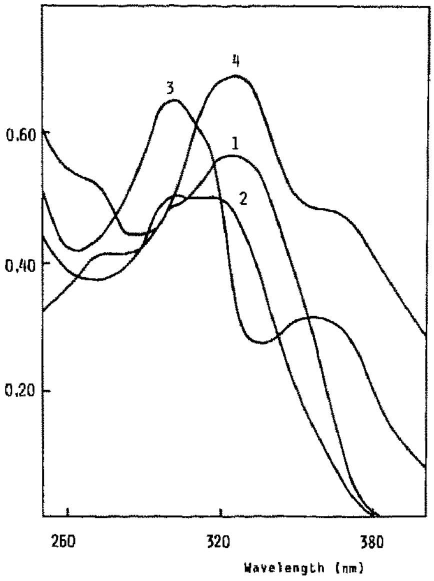


Fig. 1. Absorption spectra of PBSHB (2.5×10^{-5} M) in various solvents: (1) benzene; (2) chloroform; (3) anhydrous acetic acid; (4) isoamyl alcohol; (5) ethanol; (6) dimethylformamide; (7) water.

Fig. 2. Absorption spectra of aqueous PBSHB solutions (2.52×10^{-5} M) at different pH values: (1) pH 2.6; (2) pH 4.7; (3) pH 9.2; (4) 39.1% (w/w) perchloric acid.

posed completely after several weeks. The stability in 4 M or 2 M sodium hydroxide is only a little longer than in acidic medium of equal concentration. The stability of PBSHB in aqueous solutions is good in comparison with that of related aroylhydrazones. This can be attributed to the presence of the sulphonic group in the benzene ring which favours the formation of a ring by intramolecular bonds involving the —C=N— group.

Reducing agents (hydrazine, hydroxylamine, sulphite, ascorbic acid) and peroxydisulphate at moderate concentrations do not alter the absorption spectra of the aqueous reagent solution over a wide range of pH. However, hydroxylamine affects substantially the absorption spectra of PBSHB at pH 2.6, probably because of an exchange of C=N groups. Hydrogen peroxide slowly decomposes the reagent in all media tested.

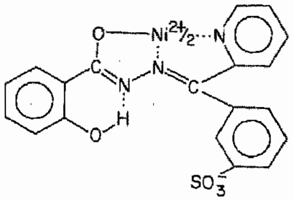
Reactions with metal ions

Among the 42 ions tested in aqueous media, a coloured reaction was observed with Pb, Cu, Cd, Pt(IV), Fe(III), V(V), rare earths, Co, Ni, Zn, Fe(II), Mn(II) and Ca. Of these ions, the most interesting are the reactions with Ni(II), Co(II) and V(V), because of their sensitivity, stability and colour contrast. None of the metal complexes of PBSHB can be extracted into methyl isobutyl ketone, iso-amyl alcohol or benzene.

Study of the reactions with nickel, cobalt and vanadium

Aqueous solutions of PBSHB react quickly with Ni(II), Co(II) and V(V) to give yellow chelates with absorption maxima located at 375 nm (Ni), 370 nm (Co) and 395 nm (V). The absorption maximum of the cobalt(II) chelate at pH 4.7 shifts slowly to 415 nm. The relative facility with which Co(II) is oxidized when it is bonded to ligands containing nitrogen donor atoms is well known. Thus, an attempt was made to evaluate the oxidation state of cobalt in the complex. When the spectrum was recorded after deaerated solutions (nitrogen stream) of reagent and cobalt(II) had been mixed, the absorption maximum (370 nm) remained unchanged for a day at least. Without these precautions, the shift to 415 nm was complete in 2 h and occurred even in the presence of ascorbic acid. In contrast, only the maximum at 415 was observed when hydrogen peroxide was added. It seems, therefore, that PBSHB reacts initially with cobalt(II) to yield a complex with maximum absorbance at 370 nm, which evolves to a cobalt(III) complex with maximum absorbance at 415 nm.

The metal-to-ligand stoichiometric ratios of the metal chelates, investigated by the continuous variations method, were found to be 1:2 for nickel and cobalt(III) and 1:1 for vanadium(V). In order to investigate the charge of the metal complexes, they were percolated through cationic (Dowex 50-X8, sodium form) and anionic (Dowex 1-X8, chloride form) exchange columns. All the metal complexes were retained on the anion-exchange resin, indicating that they are negatively charged. The Co(III) and V(V) complexes were partially retained on the cation-exchange resin, but the Ni(II) complex was not. It is apparent that PBSHB acts as a tridentate ligand in the nickel chelate, forming an octahedral complex with four five-membered rings. The exact configuration is similar to that previously established for other metal/aroylhydrazone complexes [3, 5, 8, 9].



The conditions for metal/PBSHB chelate formation were optimized for the three systems by studying all the variables affecting the complexation reactions. Optimum conditions are listed in Table 2. The cobalt/PBSHB system shows two distinct pH zones (3.7—4.0 and 5.5—6.7) of different absorbance when the pH is adjusted with dilute hydrochloric acid or sodium hydroxide solutions; the optimum pH range is 3.7—5.8 if acetate buffer is used. The optimum pH range for the vanadium chelate increased from 3.0—4.5 to 3.0—5.5 when acetate-buffered solutions were used.

Of the three chelates, only that of vanadium(V) is affected by the order of reagent addition, so that the most favourable order of addition for the

TABLE 2

Optimum conditions of formation and spectrophotometric characteristics of the chelates of Ni(II), Co(III) and V(V)

Characteristic	Ni/PBSHB	Co/PBSHB	V/PBSHB
λ_{max} (nm)	375	415	395
pH range	4.0—5.3	3.7—4.0 and 5.5—6.7(3.7—5.8)[a]	3.0—4.5(3.0—5.5)[a]
Buffer solution (ml)	Acetate (1—6)	Acetate (1—5)	Acetate (1—4) Chloroacetate (1—3)
Volume of reagent (ml)[b]	0.5—5	0.75—4	1—3
Order of addition	Immaterial	Immaterial	Metal/reagent/buffer
Ionic strength (KCl, KNO_3)	$\leqslant 0.8$	$\leqslant 0.6$	$\leqslant 0.6$
Temperature (°C)	15—50	15—25	15—50
Stability (days)	1	1	1 (pH 4.7); some h (pH 3.7)
Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)	3.6×10^4	2.7×10^4	1.4×10^4 (pH 4.7); 1.3×10^4 (pH 3.7)
Sandell sensitivity ($\mu g\ cm^{-2}$)	1.6×10^{-3}	2.2×10^{-3}	3.7×10^{-3}
Beer's law ($mg\ l^{-1}$)	0.05—2.0	0.05—1.75	0.25—5.0 (pH 4.7); 0.25—3.7 (pH 3.7)
Minimum error zone	0.32—1.26	0.5—1.5	0.7—2.7 (pH 4.7); 0.3—2.5 (pH 3.7)
Relative standard deviation	0.4	0.3	0.9 (pH 4.7); 0.7 (pH 3.7)
Hydrogen peroxide (ml)[c]	Unaffected (up to 3)	0.5—3	Affected

[a] In acetate-buffered solution. [b] Aqueous 0.1% (w/v) solution. [c] Aqueous 1% (w/v) solution.

vanadium complex was chosen for the simultaneous determination of binary mixtures of the ions. The presence of hydrogen peroxide, needed to oxidize Co(II) to Co(III), affected the formation of the vanadium complex, and had to be avoided in the case of simultaneous determination of cobalt and vanadium.

A systematic study of the interfering effects of foreign ions on the determination of 1 mg l^{-1} nickel or cobalt and 2 mg l^{-1} vanadium in acetate buffer was conducted (Table 3). The maximum metal ion/foreign ion ratio considered was 1:1000; the absorbances were measured at 375 and 385 nm for Ni, at 400 and 415 for Co, and at 395 for V. There were no appreciable differences in the perturbing effects of a given ion at either wavelengths used for nickel and cobalt and at both pH values (3.7 and 4.7) used in the determination of vanadium. At the same concentration level as the analyte, the following ions did not interfere: Hg(I), Hg(II) and Pd(II) (nickel determination); these ions plus Pt(IV), Cr(III), Sn(II) and citrate (vanadium

TABLE 3

Tolerance limits towards foreign ions in the separate determinations of nickel (1 mg l^{-1}), cobalt (1 mg l^{-1}) and vanadium (2 mg l^{-1})

Metal determined	Ions tested	Concentration tolerated (mg l^{-1})
Ni	Alkali metals, alkaline earths, Tl(I), Mg, As(III), As(V), Mo(VI), W(VI), halides, NO_3^-, ClO_4^-, SCN^-, CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, PO_4^{3-}, borate, oxalate, tartrate, citrate	1000
Co	Alkali metals, NH_4^+, F^-, Cl^-, ClO_4^-, NO_3^-, SO_4^{2-}, PO_4^{3-}	
V	Alkali metals, Ba, As(V), Cl^-, Br^-, I^-, NO_3^-, NO_2^-, CN^-, ClO_4^-, borate, CO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$	
Ni	La	500
Co	CO_3^{2-}, $S_2O_3^{2-}$, NO_2^-[a], tartrate, citrate[a]	
V	SCN^-	
Ni	Ba, Mn(II), NO_2^-	250
Co	Mg, As(III), As(V)[a], borate[a]	
V	PO_4^{3-}	
Ni	Ca[a], Br^-	100
Co	As(III), Mo(VI), Tl(I)	
Ni	Cr(III)[a], Al, Au(III), Pt(IV)	50
Co	Be[a], Sr[a], Mn(II), La, Nd, I^-, SCN^-[a], oxalate	
V	Pr, U(VI), F^-	
Co	Al[a], Pr, Rh(III), U(VI)[a], Mo(VI)[a], W(VI)[a]	25
V	Sr[a], Cd, Mn(II), Sb(III)[a], Al[a], La, tartrate	
Ni	Pb, Pr[a], Er[a], Sm[a], Sb(III)[a], Th(IV), U(VI), CN^-	10
Co	Ba[a], Cd[a], Eu[a], Sm[a], Th(IV)[a], CN^-, S^{2-}	
V	NH_4^+, Mg, Ca[a], Pb[a], Cd, Eu	
Ni	Cd, Sn(II)	5
Co	Pb[a], Tl(I)[a], Sb(III), Au(III), Pt(IV), Hg(II)	
V	Be, Th(IV), W(VI), Au(III)	

[a] Maximum concentration investigated.

determination); and Pd(II), Cr(III) and Sn(II) (cobalt determination). The ions of Zn, Bi, Cu(II), Fe, In, Ti and S^{2-} interfered at the same concentration level of Ni, Co or V. The interfering effects of these ions could be reduced for simultaneous determinations of binary mixtures of Ni, Co and V, by appropriate masking reactions with phosphate, sulphate, thiosulphate, chloride, thiocyanate or cyanide; oxalate, tartrate and citrate could be used for simultaneous determinations of cobalt and nickel.

Simultaneous determinations of binary mixtures of nickel, cobalt and vanadium

The characteristics of the Ni, Co and V systems investigated as described above permit the simultaneous evaluation of binary mixtures of these ions. Thus, the differences in the maximum absorption wavelengths of the three chelates could be utilized for the simultaneous determination of mixtures of Ni and Co, Ni and V and Co and V.

The absorption spectra of the acetate-buffered solutions, prepared as described under Experimental, with 1 mg l^{-1} nickel, 1 mg l^{-1} cobalt and 3 mg l^{-1} vanadium, in different binary combinations, are shown in Fig. 3. In all instances, the absorption spectra of the mixed complexes are the sum of the two separated complexes.

Two wavelengths of measurement were selected for each mixture: 370 and 415 nm for Ni and Co, 370 and 420 nm for Ni and V, and 395 and 415 nm for Co and V. To evaluate the molar absorptivities of the complexes at these wavelengths, calibration graphs were used, as shown at the top right corners of A, B and C in Fig. 3.

To determine traces of binary mixtures of metal ions, a single solution is processed as described under Experimental and the results are evaluated by solving sets of simultaneous equations.

For the Ni/Co system: $A_{370} = 3.6 \times 10^4\ C_{Ni} + 9.7 \times 10^3\ C_{Co}$

$$A_{415} = 2.7 \times 10^4\ C_{Co} + 2.9 \times 10^3\ C_{Ni}$$

For the Ni/V system: $A_{370} = 3.6 \times 10^4\ C_{Ni} + 5.6 \times 10^3\ C_V$

$$A_{420} = 6.3 \times 10^3\ C_V$$

For the Co/V system: $A_{395} = 1.4 \times 10^4\ C_{Co} + 1.4 \times 10^4\ C_V$

$$A_{415} = 2.7 \times 10^4\ C_{Co} + 7.0 \times 10^3\ C_V$$

where C_i is the unknown concentration of the pertinent metal ion. The molar absorptivities used will obviously have to be adjusted for local conditions.

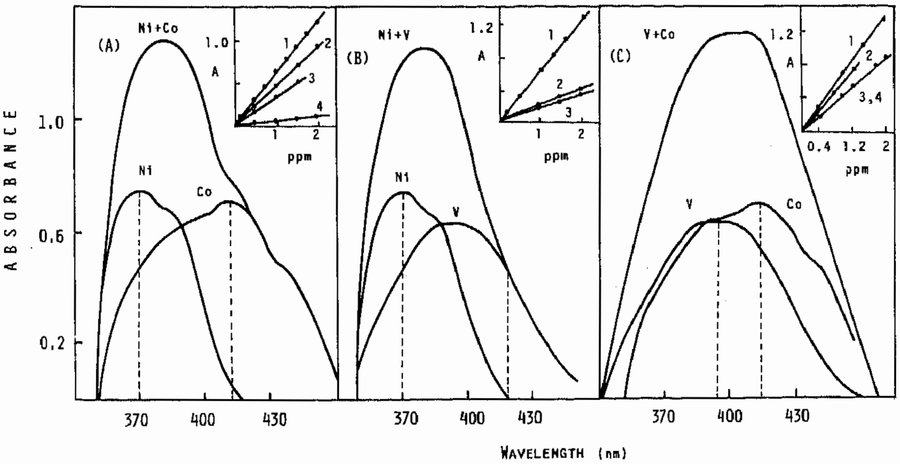


Fig. 3. Evaluation of binary mixtures of Ni, Co and V. Absorption spectra: (A) Ni, Co and Ni + Co; (B) Ni, V and Ni + V; (C) Co, V and Co + V. Calibration graphs (right top corners) for each mixture: (A) lines 1 (Ni) and 3 (Co) at 370 nm, and lines 2 (Co) and 4 (Ni) at 415 nm; (B) lines 1 (Ni) and 3 (V) at 370 nm, and line 2 (V) at 420 nm; (C) lines 1 (V) and 3 (Co) at 395 nm, and lines 2 (V) and 4 (Co) at 415 nm. Metal ion concentrations: 1 mg l^{-1} (ppm) for Ni or Co and 3 mg l^{-1} for V. Dashed lines indicate the wavelengths used for simultaneous determinations.

The results obtained in the determination of each pair of metal ions, for different metal/metal ratios, are shown in Table 4. Mixtures of Ni and Co or Ni and V can be resolved without great error for nickel/metal mass ratios ranging between 0.05 and 3—4. For the Co/V system, Co/V mass ratios must be from 0.33 to 19. It can be seen that the reported methods give satisfactory results for analyzing the binary mixtures outlined.

Conclusions

Aroylhydrazones suffer from two serious drawbacks in their use as analytical reagents. The first derives from their poor solubility in water and ethanol, which necessitates the use of large amounts of water-miscible organic solvent to prevent precipitation of the reagent in the reaction medium. The presence of the pyridine-nitrogen atom in the reagent molecule produces an insufficient

TABLE 4

Simultaneous determinations of Ni, Co and V in binary mixtures[a]

Amount taken (mg l^{-1})			Amount found (mg l^{-1})			Difference		
Ni	Co	V	Ni	Co	V	Ni	Co	V
0.10	1.90	—	0.11	2.05	—	+0.01	+0.15	—
0.20	1.80	—	0.25	1.93	—	+0.05	+0.13	—
0.40	1.60	—	0.43	1.69	—	+0.03	+0.09	—
0.50	1.50	—	0.57	1.64	—	+0.07	+0.14	—
1.00	1.00	—	1.10	0.99	—	+0.10	—0.01	—
1.30	0.70	—	1.35	0.82	—	+0.05	+0.12	—
1.50	0.50	—	1.50	0.60	—	0.0	+0.10	—
1.60	0.40	—	1.67	0.52	—	+0.07	+0.12	—
1.80	0.20	—	1.78	0.35	—	—0.02	+0.15	—
0.10	—	1.90	0.06	—	1.84	—0.04	—	—0.06
0.20	—	1.80	0.16	—	1.74	—0.04	—	—0.06
0.40	—	1.60	0.38	—	1.54	—0.02	—	—0.06
0.50	—	1.50	0.47	—	1.40	—0.03	—	—0.10
1.00	—	1.00	0.92	—	0.98	—0.08	—	—0.02
1.30	—	0.70	1.19	—	0.68	—0.11	—	—0.02
1.50	—	0.50	1.41	—	0.38	—0.09	—	—0.12
1.60	—	0.40	1.48	—	0.26	—0.12	—	—0.14
1.80	—	0.20	1.64	—	0.06	—0.16	—	—0.14
1.90	—	0.10	1.62	—	0.38	—0.28	—	—0.28
—	0.20	1.80	—	0.55	1.55	—	+0.35	—0.25
—	0.50	1.50	—	0.42	1.30	—	—0.08	—0.20
—	1.00	1.00	—	1.13	0.90	—	+0.13	—0.10
—	1.30	0.70	—	1.34	0.73	—	+0.04	+0.03
—	1.50	0.50	—	1.44	0.42	—	—0.06	—0.08
—	1.60	0.40	—	1.66	0.37	—	+0.06	—0.03
—	1.80	0.20	—	1.84	0.13	—	+0.04	—0.07
—	1.90	0.10	—	1.86	0.06	—	—0.04	—0.04

[a] Each result is the mean of three separate determinations.

increase in solubility; sulphonation of the reagent helps to solve the problem, as it has done for many other reagents. The second drawback stems from the hydrolytic reactions that these reagents undergo in acidic aqueous solutions which implies decomposition of the reagent and, in some cases, formation of metal chelates of low stability. This can be avoided by making the —C=N— group participate in a ring, as happens when pyridoxal or a sulphonated derivative is used for the synthesis of the aroylhydrazone compounds.

Despite these drawbacks, the colour reactions of aroylhydrazones with various cations present attractive sensitivities and therefore the attainment of a degree of selectivity is of interest. The new salicyloylhydrazone derived from 3-picolinoylbenzenesulphonic acid produces anionic metal complexes, which circumvent the solubility problems arising from the use of analogous reagents. Although the extensive complexing ability of the =N—C—C=N—NH—CO— grouping for metal ions still imposes some limitations on the use of these reagents, the new reagent described above yields metal chelates that can be differentiated in suitable cases. This feature has been utilized to establish spectrophotometric procedures for the simultaneous determination of binary mixtures of nickel, cobalt and vanadium that are more sensitive and selective than other methods previously reported for related compounds [23—25].

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