Analytical Study of Bis(aroylhydrazones) of 2,6-Diacetylpyridine: Application to the Spectrophotometric Determination of Antimony in Non-ferrous alloys

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The properties of 2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone) (DAPBSH) and 2,6-diacetylpyridine bis(benzoylhydrazone) (DAPBBH) are described. The reaction between Sb(III) ions and DAPBBH has been studied spectrophotometrically and the resulting orange - yellow Sb - DAPBBH complex extracted into 3-methylbutan-1-ol ($\varepsilon = 1.13 \times 10^4$ l mol^{-1} cm^{-1} at 405 nm) from pH 0.5 to 5.3. The Sandell sensitivity is 0.0011 µg cm^{-2} in 50 ml of aqueous solution. The method described is highly selective and has been applied satisfactorily to the determination of antimony in non-ferrous alloys.

Keywords: *Bis(aroylhydrazone) reagents; antimony determination; extraction; spectrophotometry; non-ferrous alloys*

The condensation products of pyridinic aldehydes or ketones with hydrazides have proved to be good chromogenic reagents.[1] The chelating behaviour of monoaroylhydrazones of some pyridine carbonyl derivatives towards metal ions has previously been examined and it has been found that salicyloylhydrazones and benzoylhydrazones are excellent organic reagents for the spectrophotometric determination of vanadium(V) and iron(II).[2-5] The introduction of a double hydrazidic chain in pyridine dicarbonyl derivatives gives rise to the formation of reagents with similar characteristics, provided that both chains can rotate freely.[6,7] Among these ligands, the behaviour of 2,6-diacetylpyridine bis(aroylhydrazones) is noteworthy owing to their tendency to produce stereochemistries of high coordination number.[8,9] It seemed appropriate, therefore, to study this family of reagents further.

This paper describes the investigation of the analytical properties of 2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone) (DAPBSH) and 2,6-diacetylpyridine bis(benzoylhydrazone) (DAPBBH). Using the latter reagent, an extraction - spectrophotometric procedure for the determination of Sb(III) has been developed in which the Sb - DAPBBH complex is extracted into 3-methylbutan-1-ol from strongly acidic media in which other metal - DAPBBH complexes are not completely formed. The proposed method has been applied satisfactorily to the determination of Sb in several standard samples of non-ferrous alloys.

Experimental

Apparatus

A Pye Unicam SP8-200 and a Perkin-Elmer Coleman 575 spectrophotometer with 1-cm optical path cells were used in the ultraviolet and visible region of the spectrum. A Metrohm Herisau Titriskop E-516 pH meter with glass - calomel electrodes was employed for pH measurements and an Apple II desk-top computer was utilised for the evaluation of analytical data.

Reagents

All solutions were prepared with analytical reagent-grade reagents using distilled water, unless stated otherwise.

2,6-Diacetylpyridine bis(2-hydroxybenzoylhydrazone) and bis(benzoylhydrazone) solutions, 0.05% *m/V*. Prepared by dissolving appropriate amounts of the reagents in dimethylformamide (DMF), dimethyl sulphoxide (DMSO) or 3-methylbutan-1-ol. A 0.1% *m/V* solution of DAPBBH in 3-methylbutan-1-ol was also used.

Antimony standard solution, 1.000 g l^{-1}. Prepared by dissolving antimony(III) chloride in 2 N hydrochloric acid and standardising titrimetrically.[10] Working standard solutions were prepared daily from this stock solution.

Procedure for the Direct Determination of Antimony

To 50 ml of sample solution in a separating funnel, containing up to 60 µg of antimony, add 0.5 ml of concentrated perchloric or nitric acid (to adjust the pH to 1) and extract with 5 ml of a 0.1% *m/V* solution of DAPBBH in 3-methylbutan-1-ol by shaking for 3 min. Allow the phases to separate and transfer the upper organic phase, previously dried on anhydrous sodium sulphate, into a 5-ml calibrated flask. Measure the absorbance of the orange - yellow extract at 405 nm against water.

The calibration graph was prepared from standard solutions of Sb(III) treated in the same way.

Procedure for the Indirect Determination of Antimony

To three aliquots of the sample solution, add increasing known amounts of antimony (0, 10 and 20 µg) and apply the extraction procedure as described above. The absorbances are plotted against the concentrations for the three antimony-containing solutions of each sample. The intersection of this curve with the concentration axis is defined by $y = 0$ in the simple linear regression equation $y = ax + b$. When $y = 0$, we find $x = -b/a = C_{Sb}$, where C_{Sb} is the concentration of antimony in the sample. All parameters in the regression equation curves were calculated by the least-squares method.

Results and Discussion

Analytical Properties of the Reagents

The reagents were synthesised by the general procedure outlined for other related compounds.[4,5] The elemental analyses for C (63.91 and 67.84%), H (4.93 and 5.98%) and N (16.27 and 17.60%) contents agreed with the values calculated from the empirical formulae of DAPBSH ($C_{23}H_{21}N_5O_4$) and DAPBBH ($C_{23}H_{21}N_5O_2$), respectively. The infrared spectra of the reagents, obtained from spectroscopically pure KBr discs, are in good agreement with those obtained by Pelizzi and Pelizzi.[8]

DAPBSH and DAPBBH have a low solubility in several common solvents (Table 1), their solubilities being lower than those of pyridine-2-acetaldehyde 2-hydroxybenzoylhydrazone (PASH)[4] and benzoylhydrazone (PABH),[11] probably owing to the presence of the double hydrazidic chain. The slight solubility difference between the two reagents, as observed in Table 1, shows that the hydroxyl group makes scarcely any contribution to the solubility, presumably as a result of the formation of intramolecular hydrogen bonds. This behaviour is in agreement with the absorption band located at 2800–2500 cm^{-1} in the infrared spectrum of DAPBSH, which can be attributed to the OH stretching vibration.[4,8,9,12]

The spectral characteristics of DAPBSH and DAPBBH in different media are shown in Table 1. The change from water to other less polar solvents resulted in a bathochromic and hyperchromic shift of the main absorption band of DAPBBH. This band is probably due to an $n \rightarrow \pi^*$ transition.[12] The molar absorptivity of this band in chloroform is about twice as large as those of the PASH[4] and PABH[11] bands (λ = 323 nm, ε = 1.9×10^4 l mol^{-1} cm^{-1} and λ = 295 nm, ε = 1.9×10^4 l mol^{-1} cm^{-1}, respectively), as DAPBSH and DAPBBH are the corresponding duplicate chromophores.

Varying the pH affected the spectra of the aqueous solutions of both reagents, both showing bathochromic shifts as the pH increased, which can be assumed to be related to the extension of the π-chromophore.

The Stenström and Goldsmith[13] and Sommer[14] methods were used for the spectrophotometric determination of the ionisation constants of the reagents at 0.1 ionic strength. The average pK_1 values were found to be 2.9 ± 0.1 and 2.7 ± 0.2 for DAPBBH and DAPBSH, respectively. They may be caused by protonation of the pyridine nitrogen atom. The average pK_2 values were found to be 9.6 ± 0.2 and 7.5 ± 0.2 for DAPBBH and DAPBSH, respectively. The first p*K* may be caused by deprotonation of the CONH group and the second by deprotonation of the hydroxyl group in the benzene ring.[15]

DAPBSH and DAPBBH solutions were stable at pH 4.9, but decomposed in moderately acidic media. However, their resistance to acid hydrolysis was greater than that of related aroylhydrazones, probably because the C=N group is part of a six-membered ring.

Redox reagents (H_2O_2, N_2H_4, ascorbic acid), at concentrations of 0.5% *m*/*V*, altered the absorption spectra of the two reagents, DAPBSH being more affected than DAPBBH. Both reagents were more strongly affected by hydrogen peroxide in acidic media and by hydrazine in alkaline solutions.

The reaction features of the reagents with more than 40 species of metal ions were investigated in water - DMF and water - DMSO media at different pH values. A medium containing 50% of organic solvent was chosen because of the slight solubility of both the metal complexes and excess of reagents. The spectral characteristics of the more interesting soluble complexes are shown in Table 2. Most metal complexes were precipitated in water - DMF media or in water - DMSO at pH 4.9 for DAPBBH, whereas for DAPBSH this

Table 1. Spectral characteristics and solubilities of DAPBSH and DAPBBH in some common solvents

		DAPBSH					DAPBBH				
Solvent	*D**	λ/nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1}	λ/nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1}	Solubility/ g l^{-1}	λ/nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1}	λ/nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1}	Solubility/ g l^{-1}
Chloroform	4.8	320	3.5	—	—	N.d.†	312	3.9	—	—	0.2
4-Methylpentan-2-one	13.1	335	2.5	—	—	0.2	335	1.6	—	—	N.d.
3-Methylbutan-1-ol	14.7	320	3.2	290	2.5	1.0	340	2.5	315	2.8	0.9
Ethanol	24.3	320	4.4	280‡	2.8	0.2	335	3.8	305‡	2.9	0.1
Dimethylformamide	36.7	305	2.6	280	2.6	1.9	345	2.9	305‡	2.2	1.1
Dimethyl sulphoxide	46.7	320	3.4	290	3.0	3.2	335	2.8	305‡	2.2	4.4
Water	78.5	320	2.7	280	2.6	0.3	330	2.1	300	2.4	0.6
Water (pH 3)		300	1.0	265	1.2	—	315‡	1.4	290	1.5	—
Water (pH 4.9)§		310	1.5	275	1.6	—	315‡	2.0	290	2.4	—
Water (pH 9.2)		332	2.8	275	3.2	—	350	2.2	295	3.0	—
Water (pH 9.8)		335	2.2	280	4.1	—	360	1.8	295	3.5	—

* *D*, Dielectric constant at 25 °C, except for $CHCl_3$ at 20 °C.
† N.d., Not determined.
‡ Shoulder.
§ A shoulder is also observed at 330 nm for DAPBSH.

Table 2. Spectral characteristics of DAPBSH and DAPBBH reactions with metal ions

	DAPBSH*		DAPBBH†	
Metal ion	$\lambda_{max.}$/nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1}	$\lambda_{max.}$/nm	$\varepsilon \times 10^{-4}$/ l mol^{-1} cm^{-1}
Bi(III)	412	34.1	380	18.6
Ca(II)	412	6.6	—	—
Cd(II)	410	12.4	385	14.2
Co(II)	410	4.2	403	5.6
Cu(II)	422	5.6	—	—
Fe(II)	420	7.2	430	1.3
Fe(III)	420	6.3	415	10.4
Hg(I)	410	10.4	400	9.8
Hg(II)	408	2.6	—	—
La(III)	408	12.3	—	—
Ni(II)	407	4.3	—	—
Pb(II)	407	15.8	403	8.2
Mn(II)	—	—	400	7.2
Sb(III)	—	—	403	1.6
Th(IV)	—	—	385	8.7

* In water - DMF (1 + 1) (pH 4.7).
† In water - dimethyl sulphoxide (1 + 1) (pH 9.2).

occurred in water - DMSO media or in water - DMF at pH 9.2. Most of the metal chelates formed by both reagents were decomposed more or less readily as the hydrogen ion concentration was increased. However, the antimony chelate was stabilised by extraction into 3-methylbutan-1-ol, the sensitivity increasing if DAPBBH was used.

Study of the Sb(III) - DAPBBH System

Extraction of the antimony chelate

When a solution of DAPBBH in an organic solvent was shaken with an acidic solution of antimony(III), an orange - yellow complex was formed immediately in the organic phase. 3-Methylbutan-1-ol proved to be the best organic solvent as the resulting complex was extracted completely and with high stability. Antimony(V) did not form any extractable complex with DAPBBH. The absorption spectrum of the Sb(III) - DAPBBH chelate in 3-methylbutan-1-ol is shown in Fig. 1(*a*). This chelate was stable for at least 1 d and showed two intense absorption bands. The first, at 340 nm, can be assigned to an $n \rightarrow \pi^*$ transition in the ligand molecule, and the other at 405 nm is probably due to a metal to ligand charge transfer.[8,9,12] This latter wavelength was employed for absorbance measurements, as the reagent does not absorb at this wavelength. Maximum constant absorbances were obtained over the pH range 0.5–5.3 [Fig. 1(*b*)]. The addition of 0.2–0.5 ml of concentrated perchloric or nitric acid was sufficient to adjust the extraction pH value in both instances.

An aliquot of 10–50 ml of solution containing 20 µg of antimony(III) was extracted with 5 ml of a 0.02–0.1% *m*/*V* solution of DAPBBH in 3-methylbutan-1-ol. Extractions were quantitative (extraction efficiency higher than 94%) for a 0.1% reagent concentration, but for a reagent concentration of 0.05%, quantitative extractions were observed for V_{aq}/V_o ratios of up to 6 : 1. Therefore, 5 ml of 0.1% reagent solution was chosen as the concentration of the chelating agent-containing solution to be used. On the other hand, if the extraction was carried out with phase-volume ratios higher than 10, the extraction efficiency was less than 87%.

The extraction was complete after a shaking time of 30 s for phase-volume ratios from 2 to 6, using 5 ml of 0.05–0.1% reagent solution. For phase-volume ratios between 6 and 10, a shaking time of 2–5 min was required to achieve complete extraction if a 0.1% reagent solution was used. Therefore, a shaking time of 3 min was selected for carrying out extraction with a phase-volume ratio of 10.

The ionic strength (sodium perchlorate, nitrate or sulphate) in the aqueous phase ($I = 0.1$) did not affect the absorbance of the extracted complex. However, if sodium chloride was used, an ionic strength of up to 0.2 could be tolerated.

The stoicheiometry of the antimony chelate was determined by Irving and Pierce's method[16] using the experimental data obtained from the extraction system. Two complex species were found with formulae SbL and SbL_2.

Extraction - spectrophotometric determination of antimony

Under the optimum conditions described above, Beer's law was obeyed between 1 and 12 µg ml^{-1} of Sb(III) in the organic phase (5 ml) at 405 nm. The optimum concentration range, evaluated by Ringbom's method, was 1.5–8 µg ml^{-1} of antimony.

The orange - yellow complex gave a molar absorptivity of 1.13×10^4 l mol^{-1} cm^{-1} at 405 nm in 3-methylbutan-1-ol, the Sandell sensitivity (in 50 ml of aqueous phase) being 0.0011 µg cm^{-2}. The mean values for eleven samples each containing 20 µg of antimony gave a relative error for the method of ±0.51%.

Antimony (20 µg per 50 ml of aqueous phase) was determined in the presence of various amounts of foreign ions. Cations and anions were added up to a maximum of 0.2 g. The tolerance limits for several ionic species were substantially increased by the use of masking reactions. Table 3 shows the effects of foreign ions on the extraction - spectrophotometric determination of Sb using DAPBBH.

Applications

To test the reliability of the proposed method, it was applied to the determination of antimony in non-ferrous alloys from the Bureau of Analysed Samples Ltd. and British Chemical Standards. Leaded gunmetal, phosphor bronze and white metal were dissolved in a mixture of concentrated hydrochloric and nitric acids and water (1 + 2 + 2, *V*/*V*)[17] and duralumin was dissolved in 30 ml of 20% *m*/*V* sodium hydroxide solution and then treated with 50 ml of hydrochloric acid (1 + 1) and a few drops of hydrogen peroxide.[18]

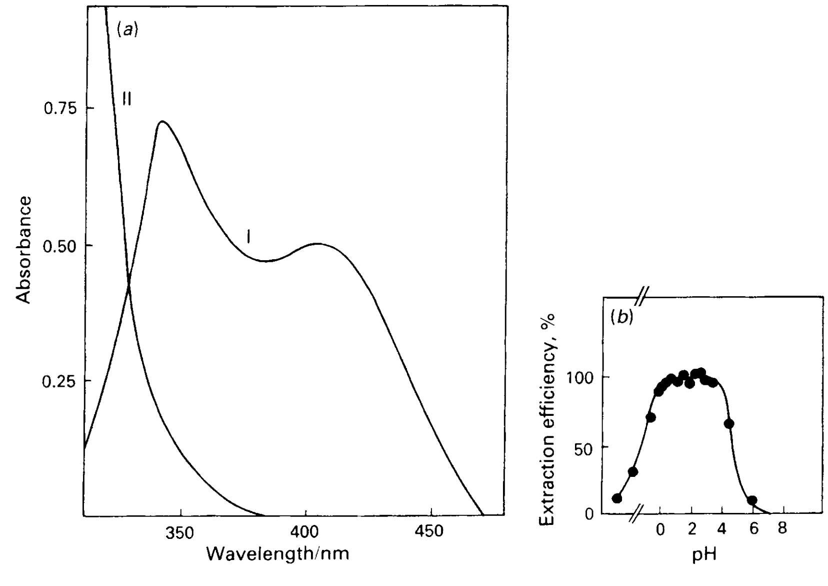

Fig. 1. (*a*) Absorption spectra of (I) Sb(III) - DAPBBH complex (3.29×10^{-5} M) and (II) reagent; (*b*) extraction efficiency *versus* pH of the antimony complex

Table 3. Interferences of foreign ions in the extraction determination of Sb with DAPBBH

Interfering species: Without masking reaction	Interfering species: With masking reaction*	Tolerated level (ion: Sb mass ratio)
Ba, Sr, Mg, citrate, PO_4^{3-}, Br^-, SO_4^{2-}, CO_3^{2-} CN^-, N_2H_4, NH_2OH, chloroacetate, Al^{3+}, Cl^-, acetate, NO_3^-, SO_3^{2-}, ClO_4^-, alkali metals	Ca, Be, Pb, Th(IV) (SO_4^{2-}); tartrate, oxalate, PO_4^{3-} (Ba^{2+}); Tl(I) (Cl^-); I^- (oxidation to I_2); NO_2^- (NH_4^+); ClO_3^- (H^+); $S_2O_8^{2-}$ (reduction to SO_4^{2-}); Hg(II) (CN^-)	10 000
Ni, La(III), Cr(III), Th(IV), As(V), $B_4O_7^{2-}$	Co (CN^-); Fe(III) (PO_4^{3-}); Fe(II) (oxidation to Fe^{3+}); BrO_3^- (reduction to Br_2); $S_2O_3^{2-}$ (H^+)	5 000
Ca, tartrate, oxalate, I^-, H_2O_2, Cu(II), Hg(II), Tl(I), Se(IV)	Au(III), Pd(II), Ag(I) (CN^-); Ti(IV), Zr(IV) (PO_4^{3-}); F^- (Al^{3+}); Hg(II) (EDTA)	1 000
SCN^-, EDTA, IO_3^-, As(III), Be, SiO_3^{2-}		500
F^-, NO_2^-, ClO_3^-, Mn(II), Nd(III), Pr(III)		250
Ag(I), IO_4^-, Co(II), Sm(III), Yb(III), Er(III)	S^{2-} (HNO_3); Bi(III) (EDTA)	100
Zn(II), Mo(VI)		50
Cd(II), Sn(II), W(VI)	Ce(IV) (EDTA)	25
Ce(IV), Zr(IV), Au(III), Fe(III)		10
Ti(IV), V(V)		2.5
Fe(II), Bi(III), U(VI), $S_2O_3^{2-}$, $S_2O_8^{2-}$, BrO_3^-, S^{2-}		1

* Masking reagent used is shown in parentheses. If a precipitate appears in the organic phase, centrifuge or filter before measuring the absorbance.

Table 4. Analysis of non-ferrous alloys

Sample	Mass/g	Antimony content, %: Found	Antimony content, %: Average found	Antimony content, %: Certified
White metal* (BAS No. 8e)	0.7601	9.49 ± 0.05	9.56 ± 0.09	9.5
	0.3754	9.63 ± 0.07		
Leaded gunmetal (BAS No. 77a)	0.4065	0.234 ± 0.008	0.241 ± 0.010	0.24
	0.8435	0.246 ± 0.010		
	0.7239	0.245 ± 0.007		
Phosphor bronze† (BAS No. 7a)	0.8690	0.064 ± 0.001	0.070 ± 0.002	0.07
	0.8698	0.077 ± 0.002		
Duralumin (BCS No. 216/2)	0.8255‡	0.033 ± 0.003	0.028 ± 0.008	0.03
	0.8333‡	0.028 ± 0.001		
	0.7341‡	0.026 ± 0.002		
	1.1831‡	0.027 ± 0.003		
	0.8928‡	0.032 ± 0.001		
	1.1831†	0.027 ± 0.007		

* Direct method.
† In the presence of EDTA.
‡ In the presence of phosphate.

The standard additions method was employed in all instances (all regression curves were almost linear, the correlation coefficients being 0.993 or higher), except for white metal. In order to prevent interferences due to foreign ions, 50 mg of phosphate or 25 mg of EDTA were added to solutions of duralumin or phosphor bronze. The results obtained for the triplicate analysis of different aliquots of different sample solutions are shown in Table 4. These data demonstrate the precision and reliability of the proposed method for the determination of antimony in the analysed samples.

Conclusion

Other methods are available for the photometric determination of trace amounts of antimony, but many of them lack high sensitivity and selectivity. This paper describes a study of the optimum conditions for a sensitive and selective spectrophotometric procedure for the determination of antimony in non-ferrous alloys. The method is free from interferences because most metallic chelates of DAPBBH are not extracted into 3-methylbutan-1-ol from strongly acidic media. The good results obtained by using masking reactions are due to the fact that the precipitates formed usually remain in the lower aqueous phase. On the other hand, the DAPBBH method may be applied to the determination of Sb at the micrograms to nanograms per millilitre level, provided optimum higher phase-volume ratios are taken, thereafter applying the standard additions method.[4]

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