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Spectrophotometric studies and applications for the determination of yttrium in pure and in nickel base alloys

A.S. Amin [a], T.Y. Mohammed [a],*, A.A. Mousa [b]

[a] *Chemistry Department, Faculty of Science, Benha University, Benha, Egypt*
[b] *National Research Center, Tahrir St., Dokki, Cairo, Egypt*

Abstract

Yttrium reacts with 5-(4′-chlorophenylazo)-6-hydroxypyrimidine-2,4-dione (I), 5-(2′-bromophenylazo)-6-hydroxy-pyrimidine-2,4-dione (II), 5-(2′,4′-dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione (III), 5-(4′-nitro-2′,6′-dichloro-phenylazo)-6-hydroxypyrimidine-2,4-dione (IV), 5-(2′-methyl-4′-hydroxyphenylazo)-6-hydroxypyrimidine-2,4-dione (V) to form a dark pink complexes, having an absorption maximum at 610, 577, 596, 567 and 585 nm, respectively. The complex formation was completed spontaneously in theil buffer solution and the resulting complex was stable for at least 3 h after dilution. Under the optimum conditions employed, the molar absorptivities were found to be 1.60×10^4, 1.29×10^4, 1.96×10^4, 1.45×10^4 and $1.21 \times 10^4 \, 1 \, mol^{-1} \, cm^{-1}$ and the molar ratios were (1:1) and (1:2) (M:L). The linear ranges were found within 95 μg of yttrium in 25 ml solution. One of the characteristics of the complex was its high tolerance for calcium and hence a method of separation and enrichment of microamounts of yttrium by using calcium oxalate precipitate was developed and applied to measure yttrium in nickel-base alloys. Interfering species and their elimination have been studied. The precision and recovery are both satisfactory.
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1. Introduction

Due to their excellent analytical behaviour, the bisazo reagents of chromotropic acid have been widely studied and applied in the field of spectro-photometry [1], some of these reagents can react with yttrium to form β-type complexes [2–4]. These methods can differentiate the absorption spectra of yttrium complexes from those of rare-earth element complexes so that yttrium can be measured in the presence of rare earth.

Although several procedures have been pro-posed in the last decade for direct or extraction-spectrophotometric determination of yttrium [5–10], there is a need for a simple, rapid, selective and sensitive method with faster colour develop-ment, which does not require rigid control of pH. In this paper, a detailed study on the complexation of Y^{3+} in 50% v/v methanol was carried out. The aim being to establish the optimum conditions

* Corresponding author.
E-mail address: asamin2002@hotmail.com (T.Y. Mohammed).

favouring direct spectrophotometric determination of Y^{3+} with reagents under consideration. No studies have yet been reported involving the complex of metal ions with those reagents.

2. Experimental

2.1. Chemicals and solutions

All chemicals were of analytical reagent grade, and bidistilled water (or pure methanol) was used for the preparation of solutions.

2.2. Synthesis of dyestuff

Pyrimidine azo dyes were prepared using conventional diazotisation and coupling methods [11]. A mixture of aniline derivatives 4-chloroaniline (2.55 g; 0.02 mol) (I), 2-bromoaniline (3.44 g; 0.02 mol) (II), 2,4 dimethylaniline (2.42 g; 0.02 mol) (III), 4-nitro-2,6-dichloroaniline (4.14 g; 0.02 mol) (IV) or 2-methyl-4-hydroxyaniline (2.46 g; 0.02 mol) (V), were dissolved in concentrated hydrochloric acid (4.8 ml) then cooled to $-5.0\,^{\circ}$C.

Sodium nitrite (1.38 g; 0.02 mol) dissolved in water (20 ml) was slowly added with continuous stirring over 15 min. The resulting clear diazo solution was slowly run at 0–$5.0\,^{\circ}$C into a fine suspension of barbituric acid (2.56 g; 0.02 mol) in water (300 ml) mixed with sodium carbonate (6.4 g; 0.06 mol) in water (150 ml). The pH of the mixture was adjusted to 10 during coupling, the mixture was continuous stirred at 0–$5.0\,^{\circ}$C for a further 6 h and then neutralised with dilute hydrochloric acid (10%). The precipitated dye was filtered, washed with cold water and dried at 40–$50\,^{\circ}$C. The prepared compounds were purified by crystallisation from a mixture of acetone and water. After recrystallisation from acetone and water, their purities were confirmed by elemental analysis as well as by sharp melting point, IR and ^{1}H NMR spectra. Their general structure is given below.

2.3. Reagents

Stock reagent solutions (I–V) of 2×10^{-3} M was prepared by dissolving an accurately weighed amount of the purified reagent in methanol. More dilute solutions were obtained by appropriate dilution.

A 5×10^{-3} M solution of yttrium nitrate was prepared by dissolving the required amount of the AnalaR product in bidistilled water. The metal content of the solution was determined as recommended [12]. Solutions of lower concentrations were obtained by accurate dilution. Solutions of diverse ions used for interference studies were prepared from AnalaR products of chloride, nitrate or acetate of the metal ions and sodium or potassium salts of the anions to be tested. Theil buffers of pH 2.0–11.0 were prepared as recommended earlier [13].

2.4. Apparatus

The absorption spectra of the solutions were recorded on a Perkin-Elmer lambda 3B spectrophotometer (Nor walk, CT, USA) in the range 350–750 nm using 10 mm matched stopper quartz cells. Values of pH were measured with an Orion research model 601 A/digital ionalyzer. The pH meter was calibrated regularly before use with standard buffer solutions. All measurements were performed in 50% (v/v) methanol–water at $25 \pm 2\,^{\circ}$C.

2.5. General procedure

To an aliquot containing 5.0–95 μg of yttrium in a 25 ml calibrated flask, add 5.0 ml of the optimum pH value as recorded in Table 1, 2.5 ml 2.0×10^{-3} M reagent solution and 10 ml methanol to achieve 50% (v/v) methanol:water ratio. The flask was completed to the mark with water and mixed well. The absorbance was then measured at 610, 577, 596, 567 and 585 nm using reagents I, II, III, IV and V, respectively, in a 10 mm cell against a reagent blank prepared similarly.

Table 1
Optical and regression characteristic, precision and accuracy of the proposed method

Parameter	Reagents				
	I	II	III	IV	V
pH	8.0	7.5	8.5	9.0	7.0
λ_{max} (nm)	610	577	596	567	585
Stability, (h)	5.0	4.0	8.0	6.0	3.0
Logarithmic stability constant[a]	3.91 (7.85)	3.65 (7.42)	4.15 (8.60)	4.60 (9.17)	3.70 (7.16)
Beers's law ($\mu g\ ml^{-1}$)	0.2–3.2	0.2–3.8	0.2–2.8	0.2–3.0	0.2–3.5
Ringbom range ($\mu g\ ml^{-1}$)	0.5–3.0	0.5–3.5	0.5–2.5	0.5–2.7	0.5–3.2
Detection limits[b] ($ng\ ml^{-1}$)	2.5	3.2	2.0	3.0	3.5
Determination limits[c] ($ng\ ml^{-1}$)	8.1	10.7	6.7	10.0	11.7
Molar absorptivity ($10^4\ l\ mol^{-1}\ cm^{-1}$)	1.60	1.29	1.96	1.45	1.21
Sandell sensitivity ($ng\ cm^{-2}$)	2.4	3.0	2.0	2.7	3.2
Regression analysis[d]					
Intercept (a)	−0.007	+0.011	+0.006	−0.008	+0.012
Slope (b)	0.41	0.33	0.50	0.37	0.31
Correlation coefficient (v)	0.9992	0.9996	0.9998	0.9996	0.9990
Standard deviation (S)[e] (%)	0.35	0.12	0.17	0.20	0.28
Relative standard deviation (Sr)[e] (%)	0.96	0.56	0.41	0.78	0.86
Range of error (%) (95%, confidence limit)	±0.8	±1.1	±0.6	±0.8	±1.4

[a] Values in parenthesis is the log k for 1:2 complex.
[b] $K = 3$.
[c] $K = 10$.
[d] $A = a + bC$, where C is concentration in $\mu g\ ml^{-1}$.
[e] Average of six replicate samples (concentration 4.5 $\mu g\ ml^{-1}$ of Y^{3+}).

2.6. Sample analysis

A sample of 0.5 g of nickel base alloy was weighed into a 100 ml beaker, 16 ml mixture of nitric acid and hydrochloric acid (1:3) was added to dissolve it and the mixture was heated to evaporate the solution to near dry. Bidistilled water, 20 ml, and 2.0 ml of 10% $H_2C_2O_4$ were added to the beaker. The pH value of the solution was adjusted to the range of 2.0–2.5 with (1:1) ammonia solution. After 2.0 ml of 10% calcium chloride was introduced, a small amount of calcium oxalate precipitate was formed. When the pH value of the solution continued to increase to 4.0, more precipitate formed in the solution. The solution was filtered and the precipitate was washed with water. The precipitate was redissolved from the filter paper with 2.0 ml of 1:10 HCl and filtrate was collected in 50 ml flask and diluted to the volume. Sample solution No. A-s-81, 2.0 ml, and/or 5.0 ml of No. A-s-82 samples

solution were taken into 25 ml calibrated flask, respectively, and the general procedure described above was followed.

3. Results and discussion

The absorption spectra of reagents (I–V) and their complexes with Y^{3+} are shown in (Fig. 1). The absorption maximum of reagents I, II, III, IV and V was at 494, 426, 430, 428 and 425 nm, while the yttrium complexes had a characteristic absorption band at 610, 577, 596, 567 and 585 nm, respectively, whereas the absorption of reagents was negligible. Investigations were carried out to establish the most favourable conditions to achieve maximum colour development in the quantitative determination of yttrium. The influence of each of the following variables on the reaction was tested.
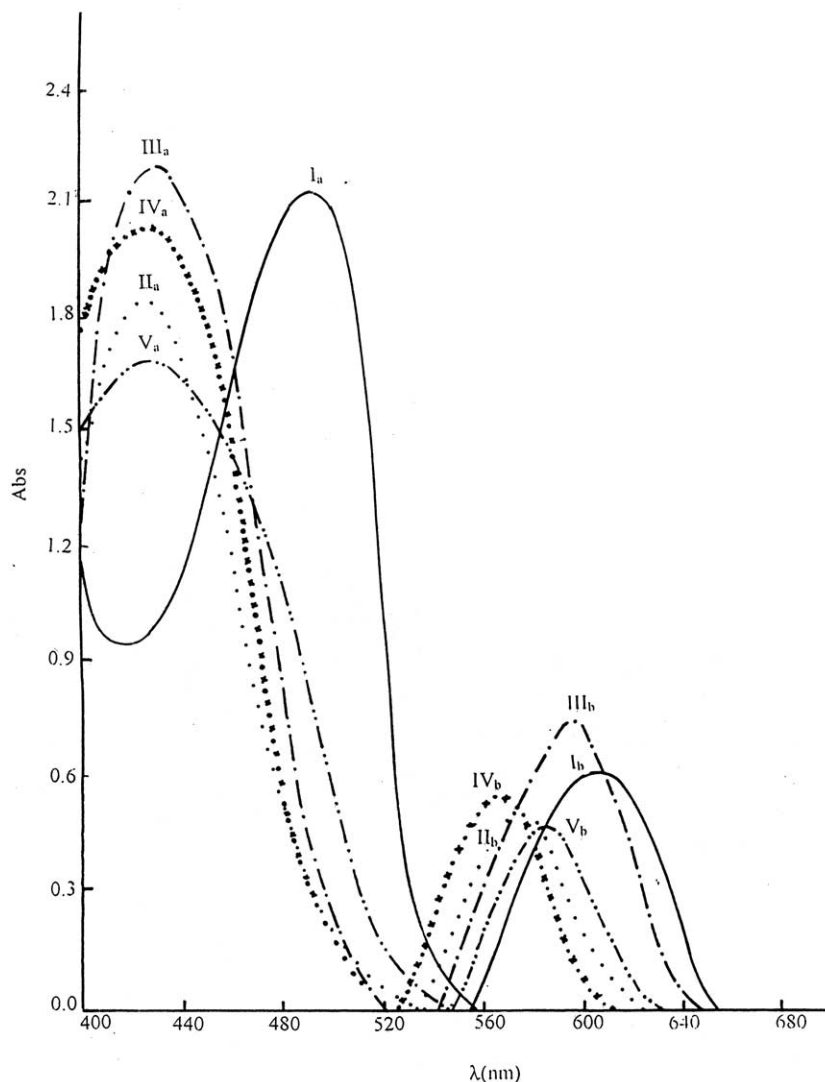
Fig. 1. Absorption spectra for (a) 2×10^{-4} M reagents (I–V) and their complexes with (b) 1.5 µg ml^{-1} Y^{3+} ions.

3.1. Effect of pH

The protonation constants of the reagents under consideration were calculated and found to be 9.63, 8.51, 10.43, 8.11 and 7.85 for reagents I, II, III, IV and V, respectively.

On varying the pH of the reaction mixture from 2.0 to 11.0 complexes with the five reagents gave maximum absorbance values in the pH ranges 7.5–8.5, 7.0–8.0, 8.0–9.0, 8.5–10 and 6.0–8.0 for I, II, III, IV and V, respectively. The absorbance-pH curves (Fig. 2) are parabolic relations, indicating that the formation of the complexes increased with increasing pH due to the decreased acidity of the medium and enhanced ionisation of the active protons of the reagents. The decrease in absorbance on the alkaline pH side is due to either the hydrolysis of the complexes or the formation of other types of hydroxoazo complexes having lower absorbance. This behaviour is quite common for complexes formed by proton displacement from reagent through the metal ion [14]. Hence, the pH
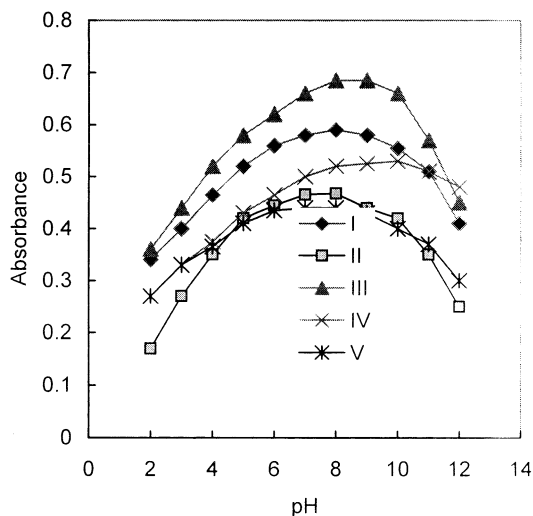
Fig. 2. Effect of pH on the colour development of the complexes of ligands (I–V) using 1.5 μg ml^{-1} Y^{3+}.

values of 8.0, 7.5, 8.5, 9.0 and 7.0 were chosen for all further studies with reagents (I–V), respectively. It was also observed that the absorbance remained constant with the addition of not more than 5.0 ml buffer solution of the optimum one in each case. Accordingly, 5.0 ml was used for all further studies.

3.2. Effect of reagent concentration

When the volume of reagent added to an aliquot of solution containing 75 μg of yttrium, was varied from 0.4 to 4.0 ml 2×10^{-3} M. The maximum absorbance was observed with the addition of 1.6 ml for complexes of I, II, and IV, whereas 2.0 ml was required for III and V complexes. Hence, 2.5 ml of 2×10^{-3} M reagent solution was employed for all further studies.

3.3. Effect of solvent ratio

Methanol was found to be the best solvent of the examined (methanol, ethanol, propanol, acetone and dioxane) to dissolve the slightly soluble yttrium complexes and the maximum absorbance was observed in the presence of 40–50% (v/v) methanol. At least 10 ml of methanol was required for the dissolution of the complex and the

absorbance decreased with the addition of more than 15 ml. All measurements were, therefore, made in the presence of 12.5 ml (50% v/v) of methanol.

3.4. Effect of surfactants

Generally speaking, introduction of surfactant can improve sensitivity and/or selectivity of the coloured complexes between rare-earth elements and bisazo reagents of chromotropic acid by forming colloid bundles. Here, effect of surfactants was tested. An appropriate surfactant was not found to improve the analytical characteristics of the studied complexes. For instance, introducing animal glue can cause the solution turbid, adding cetylpyridinium bromide (CPB) resulted in precipitate whereas using Triton X-100 or Tween-80 impeded the complexes to form.

3.5. Order of additions

Additions in the sequence 'yttrium-buffer-reagent-methanol' gave the highest absorbance values for all studied complexes. Other sequence gave the same λ_{max} with lower absorbance. Hence, the first sequence of additions was chosen as the optimum one.

3.6. Stability of the complex

The prepared colour solutions were kept in small volumes (not more than 20 ml) to stand for different time before dilution to 25 ml, then diluted and recorded their absorbances. The results indicated that all complexes are formed instantaneously with full colour developments and kept constants for 5, 4, 8, 6 and 3 h on using reagents I–V, respectively.

3.7. Composition of the complex

Under the optimum conditions of pH, reagent concentration, solvent ratio and sequence of additions described above, the metal:reagent ratios were found to be (1:1) and (1:2) (M:R) using Job's continuous variation and molar ratio methods. The conditional formation constants (log k), cal-

culating using the Harvey–Manning equation [15], for (1:1) complexes were found to be 3.91, 3.65, 4.15, 4.60 and 3.70, respectively, while the true constants were 4.00, 3.70, 4.25, 4.70 and 3.75, respectively. For (1:2) complexes, the conditional formation constants amount to be 7.85, 7.42, 8.60, 9.17 and 7.16 for reagents I, II, III, IV and V, while the true constants were 7.95, 7.50, 8.70, 9.25 and 7.30. The values indicated that the stability of the complexes increases in the order IV > III > I > II > V.

3.8. Calibration graph and reproducibility

Under the favourable conditions cited above, a linear calibration graph for Y^{3+}-reagents (I–V) systems were obtained up to a concentration ranges recorded in Table 1. A Ringbom plot showed that the optimum working range for the determination of Y^{3+} was in the range 0.5–3.5 μg ml^{-1}. The standard deviation of the absorbance measurements was obtained from a series of 13 blank solution. The limits of detection (K = 3) and of determination (K = 10) of the method were established according to the IUPAC definitions ($C_1 = KS_o/s$) where C_1 is the limit of detection, S_o the standard error of blank determination, s the slope of the standard curve and K the constant related to the confidence interval [16] and the values were calculated and recorded in Table 1. The molar absorptivity and Sandell's sensitivity calculated from increments on the slope of the calibration graph were calculated and recorded in Table 1. Ten replicate analysis of a test solution containing 1.5 μg ml^{-1} of Y^{3+} by the proposed method applying reagents I–V gave a mean standard deviations (S.D.) of 0.0037, 0.0028, 0.0041, 0.0023 and 0.0053 and a relative standard deviation of 0.93, 0.70, 1.03, 0.55 and 1.33%, respectively.

3.9. Effect of foreign ions

Coloured solutions containing 1.5 μg ml^{-1} of yttrium and various amounts of foreign ions were prepared and follow the determination procedure. If an error of $\pm 3.0\%$ was considered tolerable, the tolerance limits of foreign ions were listed in Table

Table 2
Tolerance limits for foreign ions in the determination of 4.50 μg ml^{-1} of Y^{3+}

Ion	Tolerance limits (μg ml^{-1})
K^+, Na^+	12 000
NH_4^+, Cl^-	10 000
SO_4^{2-}, NO_3^-	8500
PO_4^{3-}, CH_3COO^-	7500
Oxalate, succinate	6000
Citrate, benzoate	5000
Ca^{2+}, Sr^{2+}, Ba^{2+}	3000
Ni^{2+}, Fe^{2+}	1250
Mg^{2+}, Mn^{2+}	800
Co^{2+}, Cd^{2+}	500
Pb^{2+}, Pt^{2+}, Pd^{2+}	200
Bi^{3+}, Al^{3+}	50
Fe^{3+}, Cr^{3+}	20
Zn^{2+}, Cu^{2+}	8
La^{3+}, Sc^{3+}	5
Eu^{3+}, Gd^{3+}	3

2. There were low tolerances for rare-earth elements but Ca^{2+} had a higher tolerance limit. So a method of separation and enrichment of micro-amounts of yttrium was established by using the co-precipitate of yttrium and calcium oxalate.

3.10. Analytical application

In order to confirm the usefulness of the proposed method, it has been applied to the determination of yttrium in nickel-base alloys. Yttrium in six samples of A-s-81 and A-s-82 nickel-base alloys was determined. For A-s-81 sample, the percentage of mean yttrium content found in six determinations was 0.0444, 0.0451, 0.0466, 0.0455 and 0.0440 (standard value, 0.046) and relative standard deviations were 0.95, 1.12, 0.75, 0.88 and 1.40% on using reagents I, II, III, IV and V, respectively. On the other hand, for A-s-82 sample, the percentage of mean yttrium content found was, 0.0098, 0.0104, 0.0102, 0.0106, and 0.0094, (standard value, 0.01) and relative standard deviations were 0.85, 1.20, 0.75, 1.05 and 1.45%, respectively. As the yttrium content in No. A-s-82 sample was beyond the linear range, less amounts of this sample had to be taken.

Table 3
Comparison of spectrophotometric reagents used for determination of yttrium

Reagent	Determination range ($\mu g\ ml^{-1}$)	ε (l mol^{-1} cm^{-1})	pH	λ (nm)	References
1,4-Bis (4'-methylanilino) anthraquinone	7.12–28.5	4.60×10^3	7.7	610	[16]
Chrome Azural S, cetyltrimethylammonium	0.50–1.60	8.00×10^3	5.1	610	[2]
Pyrocatechol violet, Zephiramine	0.10–1.20	3.30×10^4	9.0	660	[2]
2-(2-Thiazolylazo)-4-methylphenol, Zephiramine	0.10–1.20	3.70×10^4	7.5	610	[17]
Purpurin (as mixed metal complexes)[a]	0.05–0.40	4.50×10^4	7.5	570	[18]
m-Carboxychlorophosphonazo[b]	0.10–0.80	1.03×10^5	2.0	669	[19]
5,8-Dihydroxy-1,4-naphthoquinone	1.95–8.86	1.15×10^4	5.5	595	[20]
m-Nitrochlorophosphonazo	0.00–6.00	8.49×10^4	6.0	731	[21]
p-Methylchlorophosphonazo	0.24–0.48	1.82×10^5	5.0	755	[7,8]
p-Nitrochlorophosphonazo	0.32–1.00	6.60×10^4	1.0	730	[9]
p-Ethoxy carbonyl chlorophosphonazo	0.24–0.56	4.48×10^4	3.5	726	[19]
p-Chloro-chlorophosphonazo	0.12–0.56	1.56×10^5	4.5	746	[6]
p-Carboxychlorophosphonazo	0.08–0.64	7.72×10^4	3.9	732	[10]
5-(4'-Chlorophenylazo-)-6-hydroxypyrimidine-2,4-dione	0.20–3.20	1.60×10^4	8.0	610	This work
5-(2'-Bromophenylazo)-6-hydroxypyrimidine-2,4-dione	0.20–3.80	1.29×10^4	7.5	577	This work
5-(2',4'-Dimethylphenylazo)-6-hydroxypyrimidine-2,4-dione	0.20–2.80	1.96×10^4	8.5	596	This work
5-(4'-Nitro-2',6'-dichlorophenylazo)-6-hydroxypyrimidine-2,4-dione	0.20–3.00	1.45×10^4	9.0	567	This work
5-(2'-Methyl-4'-hydroxy phenylazo)-6-hydroxypyrimidine-2,4-dione	0.20–3.50	1.21×10^4	7.0	585	This work

[a] By solvent extraction.
[b] Total rare earth elements.

3.11. Comparison with other methods

The proposed method is simple, rapid and yields a dark pink complexes, which is stable for at least 3 h. In this method, yttrium can be determined directly in aqueous methanol solution without the need for extraction into organic solvent. The method described here is highly selective and sensitive and is comparable to other methods for the direct spectrophotometric determination of yttrium. The sensitivities of other methods are listed in Table 3.

4. Conclusion

The results obtained above indicated that the proposed method described for the spectrophotometric determination of yttrium ions is quite rapid, precise, sensitive and selective. Thus the chromogenic reagents utilised in the described method can

safely be used under the proper conditions for the satisfactory analysis of yttrium ion in solution. Although the proposed method offers a selectivity less than that of the previously recommended methods [7–10,17–19], it showed a wider range of determination without solvent extraction or determination with other rare earth metals, so higher selectivity than them. The proposed method was successfully applied to determine yttrium in nickel base alloy samples.

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