

given in Table 1. The stabilities followed the expected Irving-William sequence⁷: $\text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+}$. No evidence for the formation of any 1:2 complex was obtained. Thus, the apparent absorbance of mixture of metal ion solutions loaded with excess of ligand could always be explained as an additive function of the absorbance of 1:1 complex and the free ligand.

To confirm the above, specially for Cu^{2+} , for which a few workers have reported the formation of 1:2 complex, conductance studies by Job's method⁸ of continuous variation were undertaken. A definite fairly sharp peak for the formation of only 1:1 complex was obtained.

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References

1. SAVELY, F. A. & FERNELIUS, W. C., *Science*, **117** (1953), 15.
2. GRIESS, P., *Ber.* **11** (1878), 2196.
3. VOGEL, A. I., *Quantitative inorganic analysis* (Longman, London), 1951, 279, 318; 337.
4. ALBERT, A. & SERGEANT, E. P., *The determination of ionization constants* (Chapman & Hall, London), 1971, 45; 85; 89.
5. JANSSEN, M. J., *Recl. trav. chim.*, **75** (1956), 1397; *J. inorg. nucl. chem.*, **8** (1958), 340.
6. MAHALINGAM, C. & SHARMA, D. D., (unpublished work).
7. IRVING, H. & WILLIAMS, R. J. P., *Nature*, **162** (1948), 746; *J. chem. Soc.*, (1953) 3192.
8. JOB, P., *Ann. Chim.*, **9** (1928), 113.

Spectrophotometric Determination of Aluminium with 2,4-Dihydroxyacetophenone Isonicotinoyl Hydrazone†

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Aluminium forms a yellow coloured soluble 1:1 complex with 2,4-dihydroxyacetophenone isonicotinoyl hydrazone (RPINH) at pH 4.5. The system obeys Beer's law over the range 0.1-1.3 $\mu\text{g/ml}$ of Al at 370 nm. The molar absorptivity and Sandell's photometric sensitivity are 2.5×10^4 litre mole⁻¹ cm⁻¹ and 0.001 $\mu\text{g cm}^{-2}$ respectively. An indirect method for the determination of fluoride in the range 0.3 to 1.3 $\mu\text{g/ml}$ is also proposed.

IT is observed that an ethanolic solution of 2,4-dihydroxyacetophenone isonicotinoyl hydrazone (resacetophenone isoniazid hydrazone, abbreviated as RPINH) is shown to give a yellow colour

when mixed with a solution of aluminium (0.1 to 1.7 $\mu\text{g/ml}$) in acetate-phthalate buffer of pH 4.5 showing maximum absorbance in the range 370-400 nm. This colour intensity decreases linearly with the addition of fluoride. Though the yellow colour is developed in the pH range 2-8, the reagent undergoes hydrolysis¹ below pH 4.0 and the colour is not stable beyond pH 6.0. This observation has been made use for the spectrophotometric determination of aluminium and fluoride and the method is described in this note.

A 5-fold molar excess of the reagent is adequate for full colour development. The colour formation is instantaneous and stable for more than 3 hr. Job's continuous variation, molar ratio and slope ratio methods indicated a composition of 1:1 (Al:RPINH) for the complex.

Determination of aluminium — Different aliquots containing 0.1-1.7 $\mu\text{g/ml}$ of Al and 5 ml of buffer (pH 4.5) were taken and to this added an ethanolic solution (2 ml) of RPINH ($2 \times 10^{-3}M$) and the volume made upto 25 ml with the deionised water. The absorbance was read at 370 nm against a reagent blank. A linear calibration curve was obtained in the range 0.1-1.3 $\mu\text{g/ml}$ of Al. With amounts higher than 1.3 $\mu\text{g/ml}$, the absorbance varied non-linearly with the amount. The total alcohol content showed no significant effect on the absorbance values. The molar absorptivity and Sandell's photometric sensitivity with respect to the metal ion are 2.5×10^4 litre mole⁻¹ cm⁻¹ and 0.001 $\mu\text{g cm}^{-2}$ respectively.

Effect of foreign ions — The following ions whose amounts are indicated in the parenthesis in $\mu\text{g/ml}$ do not interfere in the estimation of 0.65 μg Al/ml. K^+ (390), Na^+ (460), NH_4^+ (90), Co^{2+} (12), Cu^{2+} (13), Mn^{2+} (11), Ni^{2+} (12), Zn^{2+} (1500); Th^{4+} (23), Ce^{4+} (2), Cl^- (500), NO_3^- (310), SO_4^{2-} (1500).

Uranyl(II), iron(III), zirconium(IV), titanium(IV), vanadium(V) and chromium(VI) interfere by giving a turbidity. Oxalate, citrate and tartrate interfere even when present in small amounts.

Determination of fluoride — The indirect photometric determination of fluoride based on the above colour reaction is as follows:

Ammonium alum ($2.0 \times 10^{-4}M$; 2 ml) solution, buffer solution (pH 4.5, 5 ml) and an ethanolic solution of RPINH ($2 \times 10^{-3}M$, 1 ml) were taken in different 25 ml standard flasks. Different aliquots (0.3-1.9 $\mu\text{g/ml}$) of fluoride were added and the contents made upto the mark. The absorbance of each of the solution was read at 370 nm against the reagent blank. A linear plot was obtained between the measured absorbance and the amount of fluoride (0.3-1.3 $\mu\text{g/ml}$).

The procedure described above was repeated with the solution containing the fluoride to be determined. The absorbance read at 370 nm was used to compute the amount of fluoride from the pre-determined linear calibration curve.

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Reference

- MURALI MOHAN, K., *Studies in physical organic chemistry*, Ph.D. Thesis, SV Univ. Autonomous Post-Graduate Centre, Anantapur, 1980.

Spectrophotometric Determination of Rhodium(III) with Nitrosopyrimidinols

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4-Amino-2-methyl-5-nitrosopyrimidin-6-ol (AMNP), 4-amino-5-nitroso-2-thiopyrimidin-6-ol (ANTP), 2,4-diamino-5-nitrosopyrimidin-6-ol (DANP), 4-amino-5-nitrosopyrimidin-2,6-diol (4-ANP) and 2-amino-5-nitrosopyrimidin-4,6-diol (2-ANP) form coloured anionic complexes with rhodium(III) of the general formula $[(L-H)_2 RhCl_2]^-$ (where L is the nitrosopyrimidinol). Based on these reactions spectrophotometric procedures have been developed for the determination of the metal. Beer's law is obeyed in each case. Sensitivities of these reagents are better than those of nitrosophenols and naphthols.

COMPOUNDS containing the grouping $=C(ON)-C(OH)=$ are good coordinating agents for iron and platinum group metals and have been widely used for their microdetermination¹⁻⁴. Chelating characteristics of similar centres when present on pyrimidine ring have been studied by Singh and coworkers⁵⁻⁹. In continuation of these studies, the complexation of five nitrosopyrimidinols, viz., 4-amino-2-methyl-5-nitrosopyrimidin-6-ol (AMNP), 4-amino-5-nitroso-2-thiopyrimidin-6-ol (ANTP), 2,4-diamino-5-nitrosopyrimidin-6-ol (DANP), 4-amino-5-nitrosopyrimidin-2,6-diol (4-ANP) and 2-amino-5-nitrosopyrimidin-4,6-diol (2-ANP) with rhodium(III) is examined spectrophotometrically and results are reported in the present note. The ligands are suitable for microdetermination of the metal.

Stock solution of Rh(III) was prepared by dissolving its hydrated trichloride (Johnson Matthey) in 1 N hydrochloric acid and standardized² gravimetrically (weighing as metal) before use. The 0.01 M solutions of the ligands were prepared by dissolving appropriate amounts in water except in the case of DANP which was dissolved in 0.1 N hydrochloric acid. The pH of the solutions were adjusted with sodium acetate buffers and dilute solutions of hydrochloric acid and sodium hydroxide. All the other chemicals used were of reagent grade. Doubly distilled water was used throughout the work.

Procedure for the determination of Rh(III) with AMNP or ANTP—To a suitable aliquot of Rh(III) solution (Table 1) was added 25-fold excess of AMNP or ANTP (in solution form) and 5 ml of sodium acetate solution. The pH was adjusted to

6.0, using dilute solutions of HCl and NaOH. The solution was heated on a steam-bath for about 25 min, cooled and diluted to 10 ml. Its absorbance was measured at λ_{max} against reagent blank and metal content was calculated from a calibration curve.

Procedure for the determination of Rh(III) with DANP, 4-ANP or 2-ANP—A suitable aliquot of Rh(III) solution (Table 1) was mixed with 30-fold excess of DANP, 4-ANP or 2-ANP and 3 ml of acetate buffer of pH 4.0. The solution was heated for 25 min on a steam-bath, cooled and volume was made up to 10 ml. Its absorbance was measured at λ_{max} (Table 1) and the metal content was determined using a pre-calibrated graph.

Reactions of Rh with nitrosopyrimidinols—All the present nitrosopyrimidinols react with rhodium(III) in acetate buffer medium forming yellow complexes which have rhodium to ligand ratios of 1:2 (found by Job's method of continuous variations.) The reactions are slow at room temperature but rate increases on heating. The Rh(III) complexes are anionic in nature as they are retained by anion exchanger and pass through cation exchanger unaffected. Based on these facts and assuming the generally observed octahedral geometry for rhodium(III), the complexes can be formulated as $[(L-H)_2 RhCl_2]^-$, where L is a nitrosopyrimidinol. Non-extractability of all these complexes in organic solvents is also in agreement with this ionic formulation. The characteristics of the complexes formed and optimum conditions for the determination of rhodium are given in Table 1. Excess of reagent and heating beyond the limits indicated in Table 1 do not have any adverse effect on the absorbance of the complexes.

Effect of diverse ions— Ag^+ , Pd^{2+} , Ru^{3+} , Ir^{3+} and Pt^{4+} interfere in all cases. Tolerance limits (in ppm) of various ions in the determination of 4 ppm of rhodium are given below in parentheses following the ion (a, masked with EDTA; b, masked with F^- ; c, masked with citrate).

AMNP— F^- , Br^- , NO_3^- , SO_3^{2-} , SO_4^{2-} , BO_3^{3-} , PO_4^{3-} , $C_2O_4^{2-}$, tartrate, citrate or EDTA (250); I^- or NO_2^- (20); Mg^{2+} , Ca^{2+} , Sr^{2+} or Ba^{2+} (20); SCN^- or thiourea (10); Sn^{2+} , Mn^{2+} , Zn^{2+} , Cd^{2+} , or Sb^{3+} (8); Hg^{2+} , or Cr^{3+} (5); Au^{3+} , V^{4+} or Os^{8+} (2); Fe^{2+} , Co^{2+} , Ni^{2+} or Cu^{2+} (30)^a; Fe^{3+} (50)^{b,c}. $S_2O_3^{2-}$ interferes in the determination.

ANTP— F^- , Br^- , NO_3^- , SO_3^{2-} or SO_4^{2-} (400); BO_3^{3-} , PO_4^{3-} , $C_2O_4^{2-}$, tartrate, citrate or EDTA (300); I^- or NO_2^- (50); SCN^- (10); Mg^{2+} , Ca^{2+} , Sr^{2+} , or Ba^{2+} (50); thiourea (5); Sn^{2+} , Mn^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Sb^{3+} , or Cr^{3+} (5); Au^{3+} , V^{4+} , or Os^{8+} (2); Fe^{2+} , Co^{2+} , Ni^{2+} or Cu^{2+} (40)^a; Fe^{3+} (50)^{b,c}. $S_2O_3^{2-}$ interferes in the determination.

DANP— F^- , Br^- , NO_3^- , SO_4^{2-} (1000); BO_3^{3-} , PO_4^{3-} , $C_2O_4^{2-}$, tartrate, citrate or EDTA (200); NO_2^- , I^- , Hg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , (25); SCN^- , $S_2O_3^{2-}$, thiourea, Sn^{2+} , Mn^{2+} , Zn^{2+} , Cd^{2+} , or Sb^{3+} (10); Hg^{2+} or Cr^{3+} (2); Au^{3+} , V^{4+} or Os^{8+} (1); Fe^{3+} (100)^b; Fe^{2+} , Co^{2+} , Ni^{2+} or Cu^{2+} , (20)^{a,c}.

4-ANP— F^- , Br^- , NO_3^- or SO_4^{2-} (500); BO_3^{3-} , PO_4^{3-} , $C_2O_4^{2-}$ (200); EDTA (150); tartrate or citrate (100); I^- , NO_2^- , Mg^{2+} , Ca^{2+} , Sr^{2+} , or

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