



Fig. 2 — Effect of AL on Ti-GA system

Curve	Acidity/pH	$C_{Ti} \times 10^3 M$	$C_{GA} \times 10^3 M$	AL
1	1.87N	5.0	25.0	Cit
2	1.87N	5.0	25.0	Mand
3	1.0	2.0	10.0	Cit
4	1.0	2.0	10.0	Mand
5	4.0	0.05	0.8	Succ
6	4.0	0.05	0.8	Cit
7	4.0	0.05	0.8	Mand
8	5.5	0.05	0.8	Succ
9	5.5	0.05	0.8	Cit
10	5.5	0.05	0.8	Mand

5 cm cells were used in expts 1-4

with respect to Ti and GA in the mixed complexes was inferred to be 1 : 1 as in the case of tartrate reported earlier². The X_{max} of 0.60 in the case of Cit at pH 5.5 may be due to the formation of a mixed complex to a lesser extent and the binary 1 : 3 complex of Ti and GA existing simultaneously to a significant extent, than in the case of Mand. Modified Bent and French method cannot be applied at these acidities to arrive at the composition with respect to AL.

The results of continuous variation method in the presence of Succ, which does not form mixed complexes, are of interest. The X_{max} values of 0.80 and 0.75 at pH 4.0 and 5.5 respectively in the Ti-GA binary system are not shifted even in the presence of large amounts of Succ (9, 10, 13 and 14 in Table 1). This is expected as per Gould and Vosburg⁶. The X_{max} values expected for the 1:2 and 1:3 complexes forming at these pH values are 0.67 and 0.75. From a comparison of results of continuous variation method in the presence of different AL, it is con-

cluded that dragged X_{max} is shifted from that obtained in the binary system, when mixed complex formation occurs with the AL. Since Succ is able to hold Ti in solution at pH 4.0 and still the X_{max} is at a higher value, the drag of X_{max} cannot be attributed to hydrolysis and polymerization of free metal ion. As mentioned earlier, this is attributed to the simultaneous presence of lower complexes².

References

1. ATHAVALE, V. T., KRISHNAN, C. V., RAMANATHAN, P. S. & VENKATESWARLU, CH., *Indian J. Chem.*, **10** (1972), 220.
2. KRISHNAMOORTHY, T. S., RAMANATHAN, P. S. & VENKATESWARLU, CH., *Indian J. Chem.*, **12** (1974), 642.
3. SOMMER, L. & HNILICKOVA, M. M., *Bull. Soc. chim. Fr.*, (1959), 36.
4. ATHAVALE, V. T., KRISHNAN, C. V., RAMANATHAN, P. S.) & VENKATESWARLU, CH., *Indian J. Chem.*, **8** (1970), 181.
5. ATHAVALE, V. T., KRISHNAN, C. V. & RAMANATHAN, P. S., *Indian J. Chem.*, **6** (1968), 330.
6. VOSBURGH, W. C. & GOULD, R. K., *J. Am. chem. Soc.*, **64** (1942), 1630.

Determination of Hydrazine Using Potassium Dichromate as Oxidizing Agent

M. R. MAHMOUD, I. M. ISSA, M. A. GHANDOUR & A. M. HAMMAM

Chemistry Department, Faculty of Science
University of Assiut, Assiut, Egypt

Received 27 January 1975; accepted 19 March 1975

Hydrazine is oxidized quantitatively by $K_2Cr_2O_7$ in acid solutions and the reaction involves transfer of 4 electrons. Different factors affecting the success of the volumetric and potentiometric determinations of N_2H_4 have been examined. Under the optimum conditions, amounts ranging between 0.029 and 24 mg of hydrazine or 0.14 and 52.5 mg of chromium can be determined. Cu^{2+} catalyses the reaction. A statistical analysis of the data has also been carried out.

VARIOUS methods have been employed for the determination of hydrazine using different oxidizing agents¹⁻⁵. Recently, Gopala Rao and Krishna Rao⁶ investigated the reaction between Cr(VI) and N_2H_4 in the presence of phosphoric acid.

It has been observed by us that hydrazine is oxidized quantitatively by potassium dichromate in HCl medium and this reaction has been utilized for the volumetric and potentiometric determination of hydrazine.

Hydrazine, sodium thiosulphate and potassium dichromate solutions were obtained by dissolving the AR products in doubly distilled water. Solutions of hydrazine and sodium thiosulphate were standardized by recommended procedures⁷. $CuSO_4$ (0.25M), KI (10%) and HCl (10M) solutions were prepared by dissolving CP products in doubly distilled water. Starch solution used as indicator was prepared according to the method described by Vogel⁷.

Procedure—In the volumetric method, excess potassium dichromate was added to a known volume of N_2H_4 (the ratio of dichromate varying from 1:2 to 1:25 depending upon the concentration of hydrazine) and acidity adjusted to 0.2-0.8N HCl. After 5 min, 10 ml of KI (10%) were added and solution titrated against standard sodium thio-sulphate at room temperature under proper conditions⁷. Blank titrations have shown that the reaction between N_2H_4 and $K_2Cr_2O_7$ is completed in 5 min before the addition of KI.

In the potentiometric procedure, the oxidation process involves the direct titration of N_2H_4 with $K_2Cr_2O_7$ or the reverse process at an acidity ranging between 3 and 5N HCl in the presence of 0.015M $CuSO_4$, where a sudden change in the potential indicates the end point. The titration apparatus was the same as previously described⁸.

The oxidation of N_2H_4 with excess $K_2Cr_2O_7$ was investigated at different acidities and time intervals. At lower acidities (<0.20N HCl), the reaction is slow and requires 15 to 30 min for completion. However, in 0.20 to 0.80N HCl, the reaction is completed in 5 min. Above 0.8N HCl, the volume of $K_2Cr_2O_7$ consumed is less than the theoretical value which may be due to the lowering of the reaction rate.

Under the optimum conditions, good results are obtained when the initial amount of N_2H_4 varies from 0.08 to 24 mg. Similarly amounts of chromium in the range 0.17-52.5 mg can be determined with good results.

The optimum ratio of $K_2Cr_2O_7$ to N_2H_4 depends on the amount of the latter. With higher amounts of N_2H_4 (6-24 mg), the ratio should not be less than 1.5 : 1, whereas with lower amounts (4 to 0.60 mg) the ratio should be increased to 3 : 1. Higher ratios were used for determination of micro amounts.

In the potentiometric titration of hydrazine solutions with $Cr_2O_7^{2-}$ at different acidities, the attainment of equilibrium at the Pt electrode seems to be very slow even on heating to 60°. The reaction was found to be catalysed by Cu^{2+} ions. The role played by Cu^{2+} is mainly restricted to enhance the attainment of equilibrium⁹. Cu^{2+} in the concentration range 0.01-0.025M is sufficient for successful quantitative determination of N_2H_4 by the potentiometric method. Good end points are obtained at acidities ranging from 3 to 5N HCl in the presence of 0.015M $CuSO_4$ at room temperature. At lower acidities, the equilibrium becomes more or less smooth at temperatures between 40 and 50°C and good results are obtained. The titration curves obtained are characterized by sharp inflections of the order of 280 mV per 0.1 ml $K_2Cr_2O_7$ at the end points. The potentiometric titration can be carried out safely at temperatures up to 60°, provided the optimum conditions of acidity and Cu^{2+} concentration are maintained. Amounts of N_2H_4 varying from 0.029 to 18 mg can be determined with errors not exceeding $\pm 0.50\%$. The inflection at the end point decreases with decreasing hydrazine concentration.

The reverse reaction, reduction of $K_2Cr_2O_7$ by hydrazine, is very slow at different acidities even on heating to 60°. However, the reaction proceeds

smoothly at room temperature in the presence of 0.01-0.025M $CuSO_4$ and 3-5N HCl. The titration curves are smooth and characterized by sharp inflections of the order of 225-235 mV/0.1 ml N_2H_4 at the end point. 0.35-49 mg of Cr can be estimated accurately in the presence of appropriate amount of $CuSO_4$ and 3N HCl.

The statistical analysis of the data can be considered in terms of the *t*-value and the coefficient of variation¹⁰. It was found that the *t*-value obtained from the *t*-table with 18 degrees of freedom is much larger than the *t*-calc. (0.004) at all levels of significance. Furthermore, the coefficient of variation corresponding to different amounts of N_2H_4 are less than 1%. These facts indicate that the experimental and theoretical volumes of $K_2Cr_2O_7$ consumed by N_2H_4 are not significantly different. This supports the suitability of our method for the determination of N_2H_4 .

References

1. JAMIESON, G. S., *Am. J. Soc.*, **33** (1912), 352.
2. KUTENACKER, A. & WAGNER, J., *Z. anorg. allg. Chem.* **120** (1922), 261.
3. CAY, E. J., *J. Am. chem. Soc.*, **46** (1924), 1810.
4. BENRATH, A. & RULAND, K., *Z. anorg. allg. Chem.*, **114** (1920), 267.
5. ISSA, I. M. & ISSA, R. M., *Analyt. chim. Acta*, **14** (1956), 573.
6. GOPALA RAO, G. & KRISHNA RAO, P. V., *Analyt. chem. Acta*, **65** (1973), 347.
7. VOGEL, I., *A text book of quantitative inorganic analysis* (Longmans, Green, London), 1959, 331, 336, 365.
8. TOURKY, A. R., ISSA, I. M. & AMINE, A. M., *Analyt. chem. Acta*, **10** (1954), 168.
9. ISSA, I. M., MISBAH, A. S. & HAMDY, M. H., *Microchem. J.*, **17** (1972), 604.
10. LACEY, G. L., *Statistical methods of experimentation* (Macmillan, New York), 1962.

Synergistic Effect in Solvent Extraction of Ni(II) with Benzohydroxamic Acid

B. L. HIRAN, S. N. JOSHI & G. V. BAKORE

Department of Chemistry, School of Basic Sciences & Humanities, Udaipur 313001

Received 14 January 1975; accepted 1 April 1975

The extraction of Ni(II) with benzohydroxamic acid (BHA) in the presence of pyridine or quinoline in chloroform has been investigated. Nickel is extracted as an ion pair ($NiAL^+$, where A=BHA and L=pyridine or quinoline).

BENZOHYDROXAMIC acid (BHA) has been widely used in analytical chemistry¹. It is a good extracting reagent and easy to obtain. It was, therefore, thought worthwhile to investigate the extraction of Ni (II) with BHA.

During the course of the present studies it was observed that the extraction of nickel with BHA is difficult, probably because the complex formed is either not soluble in organic solvent² or takes long time to attain equilibrium. However, in the presence of pyridine or quinoline it forms an extractable complex and extraction equilibrium is attained within 15 min.