Rapid titrimetric determination of free acidity in process samples of uranyl nitrate

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A simple titrimetric method for the rapid determination of free nitric acid associated with process stream samples of uranyl nitrate is described. The hydrolysable ions present in the samples are protected from interference by complexing them with sodium fluoride or potassium oxalate. Sodium hydroxide is used as the titrant for the free acid. A mixed indicator of Bromothymol Blue and Neutral Red with a transformation point at pH 7.2 is used for the detection of the end-point when sodium fluoride is the complexant. Another mixed indicator of Methyl Red and Methylene Blue with a transformation point at pH 5.4 is used when potassium oxalate is used as the complexant. A precision of 0.02 mol l^{-1} is attainable in both cases. The results obtained compared well with those obtained using potassium hexacyanoferrate(II) as the complexant. For samples containing larger amounts of soluble silica, potassium oxalate is preferred over sodium fluoride as the latter reacts with silica, releasing hydroxyl ions and leading to lower values of free acidity. Also, potassium oxalate is superior to sodium fluoride as it generates no corrosive analytical waste.

Uranium dioxide is the most widely used ceramic fuel in nuclear reactors and is produced from magnesium diuranate (MDU) *via* the intermediate uranyl nitrate. To achieve nuclear grade purity, impurities are effectively removed from uranyl nitrate by solvent extraction using tri-butyl phosphate (TBP) in kerosene. In order to achieve maximum extraction of the uranyl ions of the required purity into the organic phase, the free nitric acid concentration in the feed solution (UNFS) is a crucial parameter to be controlled.[1] The optimum concentration of free nitric acid in UNFS has been found to be 2–3 mol l^{-1}.[2] In purified uranyl nitrate solution (UNPS), knowledge of the free nitric acid concentration enables one to calculate the amount of ammonia required for rapid neutralisation of the acid during the equilibrium precipitation of ammonium diuranate (ADU), until the onset of the precipitate. Further, for the safe disposal of uranyl nitrate raffinate (UNR), containing 0.1–1.5 gl^{-1} of uranium, the amount of alkali required for neutralisation can be calculated from its free acidity value. The free acidity (defined as the acidity in the absence of hydrolytic interferences) of solutions containing uranium is generally determined by acid–base titration in the presence of a complexant which protects uranium and other hydrolysable metal ions from interference. Complexants such as oxalate,[3–6] sulfate,[7] citrate,[8] fluoride,[9,10] EDTA,[11] mixed oxalate and fluoride,[12] hydrogen peroxide, potassium hexacyanoferrate(II)[13] and potassium thiocyanate[14] have commonly been used. The end-point is usually detected by either potentiometry[15,16] or conductimetry.[17] However, the use of visual acid–base indicators for the detection of the end-point accelerates the determination to meet the demands of industrial laboratories handling large throughputs of samples. Our attempt to use sodium sulfate as the complexant and sodium carbonate as the titrant[16] with the aim of the simultaneous determination of free acidity and the content of uranium did not yield satisfactory results in UNFS and UNR samples owing to the presence of large amounts of impurities and in UNPS samples the end-point of the titration was not sharp. This paper describes a rapid, economical and simple titrimetric method which is suitable for routine process control operations. Two procedures, employing sodium fluoride and potassium oxalate as the complexant and mixed indicator combinations of Neutral Red–Bromothymol Blue and Methyl Red–Methylene Blue, are presented. The results are compared with those obtained in a conventional method in which potassium hexacyanoferrate(II) is used as the complexant.

Experimental

Reagents

All reagents used were of analytical-reagent grade. Methanol was obtained from Ranbaxy (SAS Nagar, India). Solutions of saturated aqueous sodium fluoride (Loba Chemie, Mumbai, India), 10% m/v potassium oxalate (Loba Chemie), and 3% m/v potassium hexacyanoferrate(II) (SD Fine Chemicals, Boisar, India) were prepared in de-mineralised water. A sodium hydroxide (Soumy Agro Tech, Secunderabad, India) solution of 0.2 mol l^{-1} was prepared by standard methods. Mixed indicators were prepared as follows.

Mixed indicator A. Neutral Red (Loba Chemie)–Bromothymol Blue (SD Fine Chemicals), equal volumes of 0.1% solutions of the indicators in ethanol were mixed. The transformation point of this indicator is at pH 7.2.

Mixed indicator B. For Methyl Red (BDH, Poole, Dorset, UK)–Methylene Blue (BDH), equal volumes of a 0.2% solution of Methyl Red and a 0.1% solution of Methylene Blue were mixed. The transformation point of this indicator is at pH 5.4.

Procedure

Free acidity using potassium hexacyanoferrate(II). A UNFS sample was diluted 20-fold. To a 10 ml aliquot of this sample, 12 ml of potassium hexacyanoferrate(II) (3% m/v) and 15 ml of methanol were added. The free acid was titrated using 0.2 mol l^{-1} sodium hydroxide standard solution with constant stirring to pH 5.5. The same procedure was followed for UNPS and UNR samples, taking 2 and 1 ml aliquots, respectively, from the undiluted samples.

Free acidity using sodium fluoride. Taking the same amount of the sample aliquots as above, 15 ml of saturated sodium fluoride and 0.5 ml of mixed indicator A were added and the acid was titrated against 0.2 mol l^{-1} sodium hydroxide solution until the colour changed from reddish pink to a permanent dark green.

Free acidity using potassium oxalate. The above procedure was adopted using 10 ml of 10% potassium oxalate and 0.5 ml of mixed indicator B. Titration was carried out till the colour changed from bluish violet to emerald green.

Determination of precision. A set of 10 measurements were carried out in an identical fashion, taking one sample in each catogory, *viz*., UNFS, UNPS and UNR. The individual values of the free acidities deviated 0.02 mol l^{-1} from the mean.

Results and discussion

A typical chemical analysis of MDU is presented in Table 1. UNFS is obtained by dissolving MDU in 60% nitric acid. This solution contains large amounts of uranyl ions and impurities that impart hydrolytic interference to the free acidity determination. Introduction of a suitable complaxant into the system that can protect these ions by suppressing their hydrolysis during the titration of the free acid is a solution to this problem. Three ligands, *viz*., potassium hexacyanoferrate(II), sodium fluoride and potassium oxalate, were studied for their suitability for free acidity determination.

Potassium hexacyanoferrate(II) forms a dark brown uranyl hexacyanoferrate(II) precipitate conforming to the equation

$$K_4[Fe(CN)_6] + 2UO_2^{2+} \rightleftharpoons UO_2[Fe(CN)_6] + 4K^+$$

Free hydrogen ions present in the solution react with excess of hexacyanoferrate(II) ions to yield the species $H_4[Fe(CN)_6]$, which is titrated by the alkali up to pH 5.5. However, a considerable amount of methanol is essential to prevent the complexes of hydrolysable ions from dissociating.[18] Prolonged inhalation of methanol is hazardous to the health of the analyst. The intense colour of the precipitate calls for potentiometric determination of the end-point and renders visual acid–base indicators unusable. Moreover, the recovery of uranium from the analytical waste involves a tedious procedure. Uranium should be precipitated by treating the waste with ammonia. The residue should be thoroughly washed, dried and calcined so as to ensure that it is free from hexacyanoferrate(II). Subsequently, the impure oxide should be dissolved in nitric acid and the solution should be mixed with UNFS for further purification procedures. Considering these disadvantages, alternative complexants were sought. This method was used here merely for the sake of comparison of the results.

Sodium fluoride forms stable, colourless complexes with most impurity ions and thereby permits the use of visual acid–base indicators for the determination of the end-point. With uranyl ions, fluoride forms a UO_2F^+ complex which is stable under the titration conditions. pH titrations in solutions containing fluoride ions are generally avoided because hydrofluoric acid formed in acidic solutions attacks the glass electrode upon prolonged use, leading to ambiguous values of free acidity.[4,19] The end point is found to occur at pH 7. Hence a mixed indicator of Neutral Red–Bromothymol Blue having the transformation point, pT, at pH 7.2 was selected for the determination of the end-point, where the colour of the indicator changes sharply from reddish pink to dark green.

Fluoride can be conveniently used for UNFS and UNPS samples. However, for UNR samples, frequently a large amount of soluble silica in the form of silicic acid is found to be present, which reacts with fluoride in accordance with the following equation:

$$Si(OH)_4 + 6F^- \rightleftharpoons SiF_6^{2-} + 4OH^-$$

The hydroxyl ions produced in this reaction pre-neutralise the acid and hence a negative bias is observed in the free acidity values. This was ascertained by treating silicic acid and sodium fluoride, the resulting product being found to be alkaline. Although UNFS samples contain silicic acid, the amount becomes insignificant when the sample is diluted prior to analysis. However, when treating the large amounts of analytical waste for the recovery of uranium, corrosive ammonium fluoride is formed as a by-product. Hence this method also is less preferable for industrial applications.

Potassium oxalate forms stable complexes with all hydrolysable ions. Oxalic acid, which is a weak acid, formed in the system is titrated. However, titrating the acid until the complete neutralisation point, *i.e.*, up to pH 8.2, results in abnormally high values of free acidity. This is attributed to the fact that the hydroxylation of the complex[20] occurs at lower pH prior to the complete neutralisation of the acid. Titration up to a pre-set pH of 5.5, equivalent to the first neutralisation pH of dibasic oxalic acid, is found to yield free acidity values that are comparable to those obtained using other ligands. A mixed indicator of Methyl Red–Methylene Blue with pT at pH 5.4 was selected for the determination of the end-point, where the colour of the indicator changes sharply from bluish violet to emerald green.

The recovery of uranium from the titration waste is easier in this case. The analytical waste can be mixed directly with UNFS. Hence this method can be conveniently applied for industrial process control operations.

Table 2 gives typical concentrations of uranium and free nitric acid in the various process streams of uranyl nitrate. The free acidity values obtained for UNFS, UNPS and UNR samples using various complexants are presented in Tables 3, 4 and 5,

Table 1 Typical chemical analysis of magnesium diuranate

Constituent	Concentration (% m/m)	Constituent	Concentration (% m/m)
U_3O_8	68.6	ThO_2	0.005
Fe_2O_3	0.44	Cl^-	0.09
SiO_2	4.11	F^-	0.02
CaO	0.90	SO_4^{2-}	1.2
MgO	10.3	CO_3^{2-}	1.6
CuO	0.004	Acid insolubles	4.6
V_2O_5	0.03	Moisture	5.4
MoO_3	< 0.01		

Table 2 Range of concentrations of uranium and free nitric acid in various process stream samples

Type of sample	Concentration of uranium/g l^{-1}	Free nitric acid/mol l^{-1}
UNF	240–300	2.0–2.5
UNPS	90–110	0.2–0.3
UNR	0.1–1.5	2–3

Table 3 Comparison of FA in UNFS samples using different complexants

Sample No.	Sample code	FA/mol l^{-1}		
		Potassium hexacyanoferrate(II)	Sodium fluoride	Potassium oxalate
1	750	3.11	3.15	3.17
2	753	2.45	2.45	2.45
3	754	2.72	2.78	2.76
4	755	2.49	2.43	2.39
5	772	2.26	2.28	2.32
6	773	1.10	1.12	1.09

Table 4 Comparison of FA in UNPS samples using different complexants

Sample No.	Sample code	FA/mol l^{-1} Potassium hexacyanoferrate(II)	Sodium fluoride	Potassium oxalate
1	737	0.29	0.28	0.26
2	739	0.27	0.26	0.24
3	732	0.25	0.25	0.24
4	722	0.26	0.24	0.24
5	711	0.29	0.28	0.28

Table 5 Comparison of FA in UNR samples using different complexants

Sample No.	Sample code	FA/mol l^{-1} Potassium hexacyanoferrate(II)	Sodium fluoride	Potassium oxalate
1	757	1.51	1.47	1.51
2	776	1.65	1.56	1.64
3	822	1.61	1.56	1.65
4	826	2.22	2.12	2.20
5	830	1.55	1.45	1.51

respectively. The values are comparable to each other. A precision of 0.02 mol l^{-1} is attainable in all cases.

Conclusion

The method proposed for the determination of free acidity in uranyl nitrate process streams for the control of operating parameters involves direct titration of the acid using sodium hydroxide. Sodium fluoride or potassium oxalate can be used to complex the hydrolytic interferences. Mixed indicators can be used for the detection of the end-point. This method is rapid, economical and sufficiently accurate for process samples.

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