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Potentiometric determination of free acidity in presence of hydrolysable ions and a sequential determination of hydrazine

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ABSTRACT

A simple potentiometric method for the determination of free acidity in presence of hydrolysable ions and sequential determination of hydrazine is developed and described. Both free acid and hydrazine are estimated from the same aliquot. In this method, free acid is titrated with standard sodium carbonate solution after the metal ions in solutions are masked with EDTA. Once the end point for the free acid is determined at pH 3.0, an aliquot of formaldehyde is added to liberate the acid equivalent to hydrazine which is then titrated with the same standard sodium carbonate solution using an automatic titration system. The described method is simple, accurate and reproducible. This method is especially applicable to all ranges of nitric acid and heavy metal ion concentration relevant to Purex process used for nuclear fuel reprocessing. The overall recovery of nitric acid is 98.9% with 1.2% relative standard deviation. Hydrazine content has also been determined in the same aliquot with a recovery of nitric acid is 99% with 2% relative standard deviation. The major advantage of the method is that generation of corrosive analytical wastes containing oxalate or sulphate is avoided. Valuable metals like uranium and plutonium can easily be recovered from analytical waste before final disposal.

1. Introduction

Free acid is usually defined as the amount of acid remained in the solution as the hydrolysable ions were removed from it [1]. Determination of the free acid in solutions containing metal ions is required for the studies of hydrolysis, polymerization and complexation of metal ions and control of acidity in separation processes such as solvent extraction, ion exchange and precipitation. In the chemical analysis required for the investigation of the characteristics of a spent fuel, free acidity of the spent fuel solution has to be determined and adjusted to separate and purify the elements to be analyzed. However, the hydrolysis of uranium and various heavy metal ions in the spent fuel solution interferes with accurate determination of free acid [2]. Most of the methods are based on the alkalimetric titration after complexing the metal ions present in solution or removing the metal ions from the solution by precipitation, ion exchange or solvent extraction without changing the free acid content to prevent hydrolysis during the titration [3,4]. Although various compexing agents have been suggested, oxalate and fluoride are usually used [2–6]. End-point of the titration can be identified by using various techniques such as visual indicators [5], derivative method [4], conductometry [7] or Gran plot [8]. Although some of these titration methods with or without complexing agents have been routine in use, efforts have also been continued for improvement of present methods and the development of new ones [9]. Hydrazine is used in nuclear fuel reprocessing both as a reducing agent and as nitrous acid scavenger. It is usually added as a “holding reductant” in the electrochemical reduction of uranium and plutonium in nitric acid medium. Actually, the presence of an optimum level of hydrazine is dictated by the fact that it prevents reoxidation of the reduced uranium and plutonium. Important point is that, hydrazine forms explosive hydrazoic acid with nitrous acid which is always present in the radiation environment of a solution containing nitric acid. As a reducing agent [10,11], hydrazine normally reacts slowly at room temperature but has reaction rates at higher temperatures rapid enough to be useful for the reduction of Pu (IV) and Np (V) [12]. The rapid reaction of hydrazine with HNO_2 is applied to the stabilization of U (IV) nitrate, ferrous sulfamate, and hydroxylamine solutions in solvent extraction and ion exchange processes for the separation of uranium, plutonium actinides and fission products. A recent application is the use of hydrazine nitrate–HNO_3–KF solutions for dissolving plutonium metal. Many of these applications involve high temperature and higher acidity where the stability of hydrazine is unknown and where the maintenance of a hydrazine concentration is critical to the success of the process [13]. In a nuclear fuel reprocessing plant, wherever hydrazine is used in partitioning or any other stage, accurate and precise knowledge of hydrazine and free acid

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concentration is very important. Hence need for a sensitive, simple and reproducible method for the determination of hydrazine is very much required.

Several methods have been described in the literature for the determination of hydrazine using different analytical techniques such as voltametry [14,15], coulometry [16,17], amperometry [18], spectrophotometry [19–23], spectrofluorimetry [24–26], titrimetry [27,28], potentiometry [29–32] and indirect methods [33]. Most of the reported methods require complicated and expensive instruments and/are time consuming. But none of these have been accomplished without generating one type or other analytical waste. The limitations of various methods mentioned were still more pronounced when real samples generated from electrolytic partitioning of uranium (IV) containing hydrazine as holding a reductant were attempted to be analyzed.

Keeping in view the need of a reliable and easy method for the sequential determination of free acid and hydrazine, the present endeavor has been made. The method described here is applicable to any system containing hydrazine and free acid. The parameters studied are not of a critical nature, the adaptation of this method, therefore poses no problem to analyze real samples be it from a nuclear fuel reprocessing plant or any other source. The methodology and technique for analyzing free acid and hydrazine is described in detail. The present method is accurate and precise for the estimation of free acid and hydrazine. Sodium carbonate primary standard is used as a titrant [34]. Therefore, frequent standardization of commonly used sodium hydroxide solution is totally avoided. Since the end point is located at pH 3, the phenomenon of cation hydrolysis is also largely controlled.

2. Experimental

2.1. Apparatus

All titrations were performed using an auto titrator Model AT-97 manufactured by Mayura Analytical Pvt. Ltd., Bangalore, India. This auto titration system consists of a motor-driven titrant dispenser, a mechanical stirrer and electrodes coupled to a pH/ion analyzer and controlled by a personal computer for automatic titration and data acquisition and processing. The titrant from the reservoir was delivered accurately through a calibrated dispenser in the titration vessel. A combination pH electrode, with glass membrane and Ag/AgCl reference electrode was used for these titrations. The glass combination electrodes were calibrated with potassium hydrogen phthalate (pH 4.02), phosphate (pH 6.86) and borax (pH 9.18) buffers.

2.2. Reagents

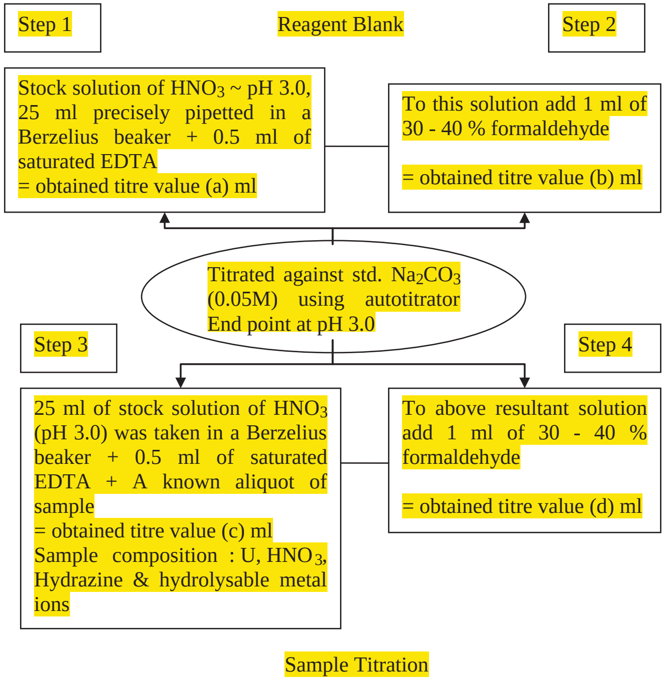
All reagents were of analytical grade and water distilled in glass distillation assembly was used throughout. Stock solutions of hydrazine (0.3–1.0 M) were prepared by diluting hydrazine nitrate, obtained from Orion Chem. Pvt. Ltd., Mumbai, in distilled water and standardized as per standard procedure [34]. Working solutions were prepared freshly every day by dilution from this stock solution. 0.05 M sodium carbonate (BDH) was prepared. Uranyl nitrate solution was prepared by dissolving recrystallized $UO_2(NO_3)_2 \cdot 6H_2O$ in distilled water. Its uranium content was determined by modified Davis and Gray procedure using potentiometric end point detection [35]. Formaldehyde obtained from Sarabhai M Chemicals Baroda, India, adjusted to pH 3.0 using standard sodium carbonate solution. Other solutions of 0.001 M nitric acid, saturated EDTA, ferric nitrate, aluminum nitrate, ceric ammonium nitrate (M/s Sarabhai M Chemicals Baroda, India) were prepared and standardized using standard described in literature [34].

3. Procedure

Simultaneous determination of free acidity and hydrazine using oxalate complexation was carried out as per the reported procedure [36,37]. In cases where titrations were performed in non-complexing medium the following method was used. Stock solution of HNO_3 of approximately pH 3 was made with the use of dilute HNO_3. 25 ml of above solution was aliquoted precisely with help of transfer pipette in a Berzelius beaker. The beaker was placed on the titrating stand of the automatic titrator. The glass electrode assembly was then lowered in this solution. The titration was completed by titrating this solution against a standard solution of sodium carbonate, which was kept in the reagent bottle of the titrating system, up to predetermined end point at pH 3.0 (a). Then added 1 ml of 30–40% formaldehyde to the same solution and again titrated with standard solution of sodium carbonate (b). This titration was repeated at least five times to find out very precisely the consumption of sodium carbonate solution in attaining the required pH. The average of these titer values was taken as reagent blank in subsequent steps (a and b).

25 ml of above-mentioned stock solution was taken in a Berzelius beaker. Accurately measured aliquot of the sample was added in to this solution. Then the titration was completed as described above (c). Then 1 ml of 30–40% HCHO was added to this solution and the generated H^+ ions were again titrated with same sodium carbonate (d). The difference between the two titer values, obtained from step (c–a) is the volume of standard sodium carbonate required to neutralize free nitric acid and the difference between step (d–b) gives the sodium carbonate solution required to react with generated H^+ ions, equivalent to the hydrazine content of the sample.

0.5 ml of saturated EDTA solution was added to the solution prior to step (a) to prevent the hydrolysis of hydrolysable ions [U(IV), U(VI), Ce(IV) Al(III) and Fe(III)] and proceeded with the titration procedures described above.



Free acidity conc. of the sample (M)

$$= \frac{(c - a) \times \text{Normality of std. } Na_2CO_3}{\text{Volume of aliquot}}$$

Table 1
Determination of free acidity in uranium and cerium samples with/without complexation.

S.no.	Amount of U and Ce taken (mg)	Free acidity (N) determined	
		With sulphate complexation, end point pH 3.7	Without complexation, end point pH 3.0
1	1.44	3.366	3.367
	&	3.321	3.346
	3.21	3.376	3.385
		3.396	3.365
		3.415	3.392
		$\Sigma = 3.375 \pm 0.035$	$\Sigma = 3.371 \pm 0.018$
2	2.88	3.342	3.405
	&	3.409	3.394
	6.42	3.398	3.299
		3.366	3.420
		3.376	3.276
		$\Sigma = 3.378 \pm 0.026$	$\Sigma = 3.379 \pm 0.06$

$$\text{Hydrazine conc. of the sample (M)} = \frac{(\text{d} - \text{b}) \times \text{Normality of std. Na}_2\text{CO}_3}{\text{Volume of aliquot}}$$

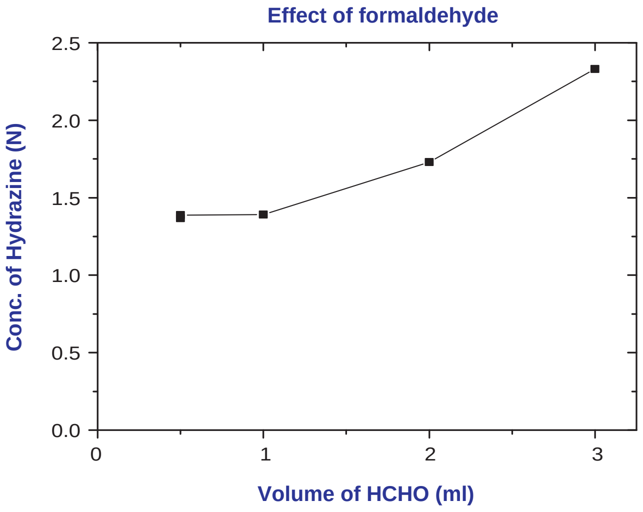


Fig. 1. Effect of formaldehyde.

4. Results and discussion

The term free acidity is defined as the concentration of acid determined for preventing the hydrolysis of hydrolysable ions present in the solutions. In case of nuclear fuel processing/reprocessing solutions it is the amount of nitric acid, which is determined, for preventing the hydrolysis of thorium, uranium, plutonium and fission products.

The present method described here is an improved version of the earlier reported procedure [38–40]. Here sodium carbonate is used as titrant in place of commonly used sodium hydroxide mainly because of two reasons. First, sodium carbonate is a primary analytical standard where as the strength of sodium hydroxide solution changes daily, which means, it needs to be standardized every day, generating additional work. Secondly the end point obtained with sodium carbonate as titrant is around pH 3.7, which largely avoids the hydrolytic interference of metal ions [41]. In consideration of these two points it is advantageous to use sodium carbonate as a titrant in place of sodium hydroxide for the determination of free acidity in presence of hydrolysable metal ions. To determine free acid in a non-complexing medium, sodium carbonate was used as titrant and titration was allowed to proceed up to the equivalence point of the system, i.e., pH 3.7. The results obtained are positively biased and the degree of bias increases with increasing uranium concentration (Table 1). This confirms that in the vicinity of pH 3.7 hydrolysis of metal ion starts, which is significant enough to interfere with the analytical result. It means the standard literature procedure of Ahmed et al. [38] if implemented as such in a non-complexing medium will yield biased results and the degree of bias will depend on the concentration of metal ions. Location of end point much before the equivalence point pH 3.7 will prevent the hydrolytic interference of metal ions but the degree of error is likely to be higher. Due to this reason it was preferred to restrict the end point to pH 3 as a reasonable compromise. Free acidity determined in solutions containing uranium/uranium and cerium in a non-complexing medium at end point pH 3 compares well within 3% with the free acidity determined where sulphate was used as complexing agent and the end point pH was 3.7. These results confirm the reasonability of the compromise on end point pH in a non-complexing medium. But in presence of hydrazine similar approach failed to yield the desired results and hydrolysis of metal ion was visible. It was then necessary to complex the metal ion with a suitable ligand to prevent hydrolysis and at the same time control corrosion in storage tanks. Figs. 1 and 2 show that typical calibration graph showing the accuracy for the determination of free acid and hydrazine by proposed method. Commonly available ligand EDTA was found to meet these two requirements and hence was chosen. The optimum concentration of EDTA was observed to be 0.5 ml of saturated EDTA solution (slightly more than the solubility of EDTA sodium salt 100 g/L) Fig. 3, and so this was used in all subsequent titrations as and when needed. This standardized procedure was

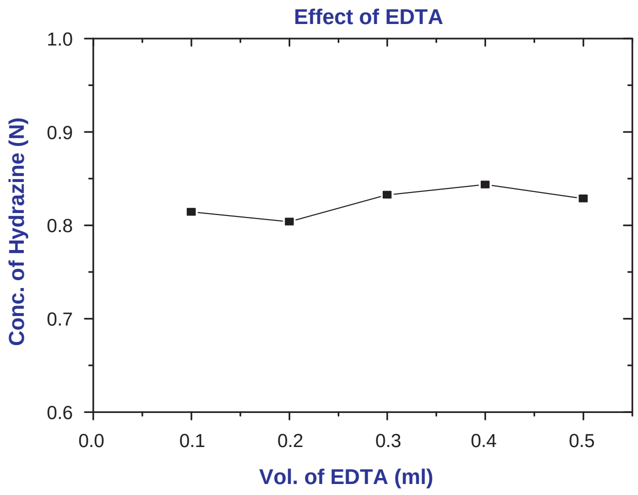


Fig. 2. Effect of EDTA.

Table 2
Effect of 30–40% formaldehyde: 25 ml of 0.001 M HNO_3 + 0.5 ml saturated EDTA + sample vs Na_2CO_3 (0.05N) + 30–40% HCHO vs Na_2CO_3 (0.05N).

S.no.	Vol. of HCHO added (ml)	Vol. of EDTA added (ml)	Normality of free acidity & hydrazine taken (N)	Amount of uranium taken (mg)	Normality of free acidity (N)	Normality of hydrazine (N)
1	0.5	0.5	2.5 & 1.4	0.375	2.463	1.368
2	0.5	0.5	2.5 & 1.4	0.375	2.497	1.388
3	1	0.5	2.5 & 1.4	0.375	2.466	1.390
4	2	0.5	2.5 & 1.4	0.375	2.470	1.730
5	3	0.5	2.5 & 1.4	0.375	2.454	2.329

Table 3
Effect of EDTA: 25 ml of 0.001 M HNO_3 + 0.5 ml saturated EDTA + sample vs Na_2CO_3 (0.05N) + 1 ml of 30–40% HCHO vs Na_2CO_3 (0.05N).

S.no.	Vol. of EDTA added (ml)	Normality of free acidity & Hydrazine taken (N)	Amount of uranium taken (mg)	Normality of free acidity (N)	Normality of hydrazine (N)
1	0.1	1.0 & 0.82	0.375	1.1280	0.8143
2	0.2	1.0 & 0.82	0.375	1.0189	0.8040
3	0.3	1.0 & 0.82	0.375	1.0302	0.8327
4	0.4	1.0 & 0.82	0.375	0.9789	0.8436
5	0.5	1.0 & 0.82	0.375	0.9492	0.8288

Table 4
Effect of metal ions: 25 ml of 0.001 M HNO_3 + 0.5 ml saturated EDTA + sample vs Na_2CO_3 (0.05N) + 1 ml of 30–40% HCHO vs Na_2CO_3 (0.05N).

S.no.	Normality of free acidity & hydrazine taken (N)	Amount of metal ion taken (mg)		Normality of (N)	
		Metal ions	Amount of metal ions	Free acidity	Hydrazine
1	1.125 & 0.925	Al(III)	10.328	1.1279	0.9126
2	1.125 & 0.925	Fe(III)	6.12	1.1372	0.9306
3	1.11 & 0.85	Ce(IV)	3.916	1.1058	0.8506
4	1.125 & 0.82	U(VI)	15	1.1755	0.8179
5	0.79 & 0.68	U(IV)	2.059	0.7906	0.6783

then applied for the determination of free acidity in stripped product sample where metal ion/H^+ ratio is the highest in Purex process. These results are fairly accurate and precise and compare well with the results obtained by the sulphate complexation procedure.

Determination of hydrazine is generally based on its reaction with formaldehyde which results in the generation of equivalent amount of acidity, as per the following equation

$$HCHO + N_2H_4{\cdot}HNO_3 \rightarrow HNO_3 + HCH{=}NNH_2 + H_2O$$

The intermediate hydrazone ($RCH{=}NNH_2$) may form, but it reacts immediately with more aldehyde to give the azine ($RCH{=}NN{=}CHR$). If excessive amount of formaldehyde is used, it forms azine, which results in the higher values of hydrazine concentration [42,43]. Optimum quantity of formaldehyde is found to be 1 ml of 30–40% HCHO; Fig. 2, where as use of higher concentration of formaldehyde resulted in unacceptable positive bias. Results of determination of free acidity and hydrazine in presence of hydrolysable metal ions like U(IV), U(VI), Fe(III), Al(III), and Ce(IV) are reported in Tables 5–6.

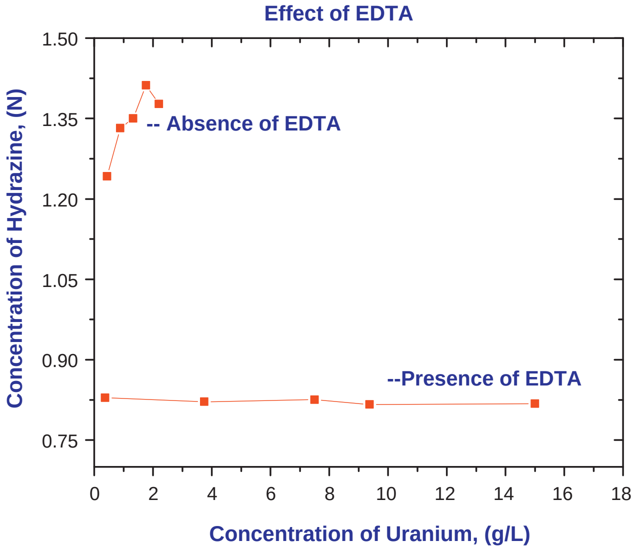


Fig. 3. Determination of hydrazine in presence/absence of saturated EDTA.

Fig. 1 provides the data on the optimum quantity of 30–40% formaldehyde needed for effective titration. In this study after acidity determination, the volume of 30% formaldehyde added to the same solution for the determination of hydrazine. For drawing this curve, different volumes of 30% HCHO were added to the sample and quantification of hydrazine. From the graph, it is obvious that 0.5 ml of 30% HCHO is enough to determine the hydrazine concentration. This quantity was found to hold good for samples containing more hydrasable metal ions. This means that hydrogen ion production is more when volume of 30% HCHO is increased. Results obtained with effect of 30% HCHO are presented in Table 2. The optimum volume of saturated EDTA required for the determination of free acid and hydrazine present in the hydrolysable ions (Fig. 2). From this it was found 0.5 ml of saturated EDTA is required if metal ions concentration is more, it will not affect because more EDTA is available in the system. If lower volume of saturated EDTA, there was no change in free acid determination but in hydrazine determination, hydrazine values are varying. These results are reported in Table 3. The curve was drawn by allowing the titration with or without saturated EDTA, and metal ion concentration is same in both titrations. From this figure (Fig. 3), in absence of saturated EDTA, the hydrazine concentration is varying depending on the metal ions. But no effect in the free acid determination step. Table 4 provides data on interference of various hydrolysable metal ions in the real sample contained hydrazine and nitric acid medium. The relative standard deviations (ten replica

Table 5
Effect of U(IV): 25 ml of 0.001 M HNO_3 + 0.5 ml saturated EDTA + sample vs Na_2CO_3 (0.05N) + 1 ml of 30–40% HCHO vs Na_2CO_3 (0.05N).

S.no.	Normality of free acidity & hydrazine taken (N)	Amount of uranium taken (mg)	Normality of free acidity (N)	Normality of hydrazine (N)
1	0.79 & 0.68	0.4118	0.8068	0.6653
2	0.79 & 0.68	1.0295	0.7727	0.6860
3	0.79 & 0.68	1.2354	0.8141	0.6808
4	0.79 & 0.68	2.0590	0.7690	0.6812

Table 6
Effect of U(VI): 25 ml of 0.001 M HNO_3 + 0.5 ml saturated EDTA + sample vs Na_2CO_3 (0.05N) + 1 ml of 30–40% HCHO vs Na_2CO_3 (0.05N).

S.no.	Normality of free acidity & hydrazine taken (N)	Amount of uranium taken (mg)	Normality of free acidity (N)	Normality of hydrazine (N)
1	1.01 & 0.82	0.375	0.9492	0.8288
2	1.2 & 1.0	3.75	1.2475	0.9973
3	1.2 & 0.82	7.5	1.2779	0.8254
4	1.2 & 0.82	9.375	1.2093	0.8163
5	1.12 & 0.82	15	1.1755	0.8179

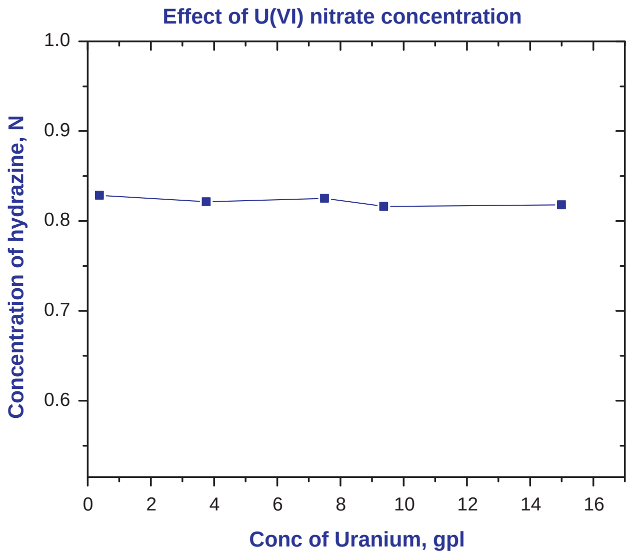


Fig. 4. Effect of metal ion concentration.

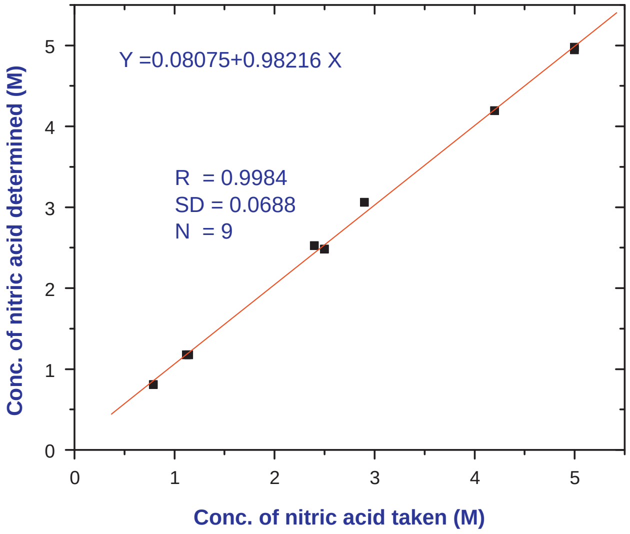


Fig. 5. Typical calibration graph showing the accuracy for the determination of free acid using this method.

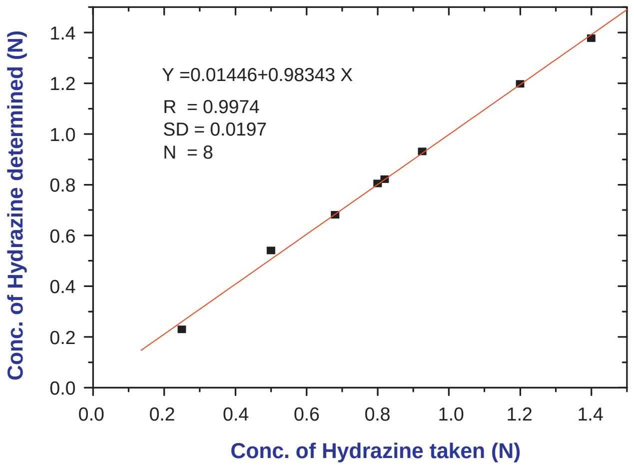


Fig. 6. Typical calibration graph showing the accuracy for the determination of hydrazine using this method.

measurements) were calculated and reported as 3%. Similarly Tables 5 and 6 represents for only U(IV) and U(VI) alone present in hydrazine and nitric acid samples. The RSD values for U(IV) and U(VI) were also calculated and reported less than 1% in both samples. From the analytical results of real as well as laboratory samples it is evident that the present method is highly precise and accurate for the simultaneous determination of free acid and hydrazine in any sample. Fig. 4 refers the effect of U(VI) nitrate, there was no change in free acidity and hydrazine determination. Calibration graph (Figs. 5 and 6) were drawn for determination of free acid and hydrazine in all range. This graph indicates very good precision and accuracy for simultaneous determination of free acid and hydrazine present in hydrolysable metal ions.

5. Conclusion

The proposed method for sequential determination of free acid and hydrazine in presence of hydrolysable metal ions is simple, sensitive and applicable to all ranges of nitric acid and heavy metal ion concentration relevant to Purex process used for nuclear fuel reprocessing. The efficacy of the developed technique for the determination of free acid and hydrazine in samples was established by comparing the results with those obtained with oxalate and sulphate [37,38] methods. The results are found to be in good agreement. The overall recovery of nitric acid is 98.9% with 1.2% relative standard deviation. The method described here for the determination of free nitric acid and hydrazine concentrations in processing/reprocessing solutions of nuclear fuels does not generate corrosive analytical waste, provides accurate and precise results and saves man-rem exposure.

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