A Study on the Alkalimetric Titration with Gran Plot in Noncomplexing Media for the Determination of Free Acid in Spent Fuel Solutions

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Received June 6, 1998

Based on the study of hydrolysis behaviour of U(VI) ion and major fission product metal ions such as Cs(I), Ce(III), Nd(III), Mo(VI), Ru(II), and Zr(IV) in the titration media, the performance of noncomplexing-alkalimetric titration method for the determination of free acid in the presence of these metal ions was investigated and its results were compared to those from the complexing methods. The free acidities could be determined as low as 0.05 meq in uranium solutions in which the molar ratio of U(VI)/H$^+$ was less than 5, when the end-point of titration was estimated by Gran plot. The biases in the determinations were less than ±1% and about +3% respectively for 0.4 meq and 0.05 meq of free acid at the U(VI)/H$^+$ molar ratio of up to 5. Applicability of this method to the determination of free acid in spent fuel solutions was confirmed by the analysis of nitric acid content in simulated spent fuel solutions and in a real spent fuel solution.

Introduction

A term, free acid, has been introduced to discriminate the strong inorganic acids, such as nitric, hydrochloric and sulfuric acid from heavy metal ions which tend to act as acids due to the hydrolysis reaction in solution.[1] Free acid is usually defined as the amount of acid remained in the solution as the hydrolyzable ions were removed from it.[2,3]

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 requisite to the investigation of the characteristics of a spent fuel (i.e. used nuclear 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 accurate determination of free acid.

When a hydrolyzable metal ion is present and its concentration is known, the free acidity can be determined by measuring the pH of the sample in a calibration curve.[4,5] Conventional alkalimetric titration methods can be used for samples containing relatively low concentration of hydrolyzable metal ions in comparison to the free acid concentration.[4] On the other hand, free acid in the presence of more hydrolyzable metal ions can not be titrated accurately, especially when the molar ratio of metal ion to free acid is relatively high.

Various methods have been suggested for the determination of free acid in uranium solutions.[4-15] Most methods are based on the alkalimetric titration after complexing the uranium in solution or removing the uranium from the solution by precipitation, ion exchange or solvent extraction without changing the free acid content to prevent hydrolysis during the titration.[6,16] Although various compexing agents have been suggested, oxalate and fluoride are usually used.[4~9]

End-point of the titration can be identified by using various techniques such as visual indicators,[8] derivative method,[4,5] conductometry[17] or Gran plot.[8,14,15] Although some of these titration methods with or without complexing agents have been routinely in use, efforts have also been continued for improvement of present methods and the development of new ones.[10,11,18]

Up to now, many studies[4-14] have been directed toward newly developed methods for the determination of nitric acid in the presence of such hydrolyzable metal ions as U(VI), Pu(IV), Th(IV), Al(III), Fe(III), Co(II), Ni(II) and Cr(III) relevant to PUREX process. However, there have been few investigations considering the effect of major fission product metal ions, like Nd(III), Ce(III), Zr(IV), Mo(VI), Ru(II) and Cs(I), on the determination of free acid. In this study, we compared the performances of noncomplexing method and two complexing methods in the presence of U(VI) ion and these fission product metal ions, for the alkalimetric titration of free acid. Further study to ascertain the applicability of these methods to the spent fuel solutions has been conducted by the determination of free acid in simulated spent fuel solutions and in a real spent fuel solution.

Experimental Section

Reagents. All reagents used in this study were of analytical reagent grade and purchased from Aldrich Chem. Co. except uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, which was obtained from Merck. The stoichiometric purity of $UO_2(NO_3)_2 \cdot 6H_2O$ was determined by thermogravimetry, which was converted to U_3O_8 by igniting at 900 °C for 7 hrs. Acidimetric titration[14,15] of $UO_2(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, $Nd(NO_3)_3 \cdot 6H_2O$, $CsNO_3$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $ZrCl_4$ showed negligible acid excess or deficiency as compared to the free acidity of test solutions. Free acidity of a ruthenium nitrosyl nitrate solution(Aldrich) was determined

by standard addition of nitric acid and subsequent alkalimetric titration. Deionized water was prepared by passing distilled water through Milli-Q system. The titrant of 0.10 N NaOH was standardized against potassium hydrogen phthalate. Nitric acid stock solutions in the concentration ranges from 0.1 to 5.0 N were prepared by diluting concentrated nitric acid with deionized water and were titrimetrically standardized with the NaOH titrant. Uranium stock solution containing 400 mg-U/mL was prepared by dissolving the weighed quantity of the uranyl nitrate hexahydrate in deionized water. Standard HNO_3-metal salt solutions were prepared by dissolving calculated amount of each metal salt and acid stock solution in deionized water. Potassium oxalate solution of 0.20 M and mixed potassium oxalate-potassium fluoride solution of 0.10 M each, were prepared by dissolving calculated amount of each compound in deionized water. All solutions were stored in polypropylene bottles.

Titration of dilute metal ion solutions. Through this study, we have used three different titration media: a noncomplexing medium of deionized water only and two complexing media of 0.20 M potassium oxalate and mixture of 0.10 M potassium oxalate and 0.10 M potassium fluoride. Aliquots of test solutions were pipetted to 40 mL of each solution and titrated with 0.10 N NaOH titrant.

Four hundred microliters of each standard HNO_3-metal salt solution and 40 mL of deionized water (*i.e.* noncomplexing method) were subsequently taken into a 100 mL polypropylene beaker and titrated with 0.10 N NaOH titrant. The titrated solution was continuously stirred, while adding the titrant manually using Metrohm 725 Dosimat equipped with a 5 mL burette. ORION model 520A pH meter and combination electrode (ORION model 81-02) were used to measure the pH of solutions. Similar titrations were performed in 40 mL of the oxalate solution and the mixed oxalate-fluoride solution. In the cases of these two complexing methods, NaOH titrant was standardized against the standard nitric acid added to each complexing medium using the same pH electrode and titration vessel as those used in the titration of samples.

Titration of uranium solutions. In order to study the effect of molar ratio of uranium to free acid, aliquots of the standard nitric acid solution and the uranium stock solution were subsequently pipetted to 40 mL of deionized water, and titrated with 0.10 N NaOH titrant. Titrations were similarly performed in the two complexing media.

Titration of simulated and real spent fuel solutions. Titrations of the various aliquots of the standard solutions containing uranium, nitric acid and fission product metal ions were carried out by the nocomplexing method and the Gran plot for the end-point prediction.[19,20] Similar titrations were also performed in the two complexing media.

Spent fuel solution was prepared by dissolving the spent fuel sample described in Table 1 with nitric acid(1:1 v/v) in a lead hot cell, and its uranium concentration was determined by the Davies-Gray method.[21] Titrations of free acid in the spent fuel solution were carried out by above mentioned three methods in a glove box.
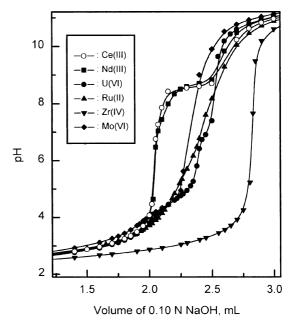
Table 1. Oxidation state and first hydrolysis constant of uranium and major fission product metal elements in spent fuel solution

Element	Content in spent fuel,[a] kg	Oxidation state in nitric acid	First hydrolysis constant,[b] pK_h
U	953.9	+6	5.8
Zr	3.805	+4	0.3
Mo	3.528	+6	
Ru	2.330	+2	
Cs	2.511	+1	~14
Ce	2.505	+3	9.7
Nd	4.257	+3	9.4

[a]Data for KORI fuel calculated by ORIGEN-2 code; original amount of uranium charged to PWR: 1000 kg; initial enrichment: 3.21%; burnup: 35,000 MWd/t; cooling time: 10 years. [b]Hydrolysis constants are equivalent to the equilibrium constants for the following hydrolysis reaction[1,23]; $xM^{n+} + yH_2O = M_x(OH)_y^{(xn-y)+} + yH^+$
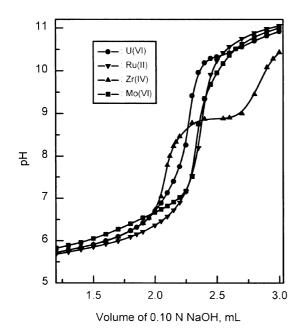
Results and Discussion

Effect of metal ions on the titration curve. Zr, Mo, Nd, Cs, Ru and Ce are present in largest amounts by molar percent and constitute approximately 60 wt% of fission products in the spent PWR (pressurized water reactor) fuel.[22] The contents of uranium and major fission product metal elements in spent fuel, their oxidation states in nitric acid solution and the first hydrolysis constants are given in Table 1. The smaller the hydrolysis constant of pK_h is, the more significantly the metal ion hydrolyzes. Alkalimetric titration of a nitric acid solution containing hydrolyzable metal ions has some complications over the analogous titration of a strong acid. Cesium as well as other alkali metal ions does not nearly hydrolyze. As can be seen from Table 1, the lan-
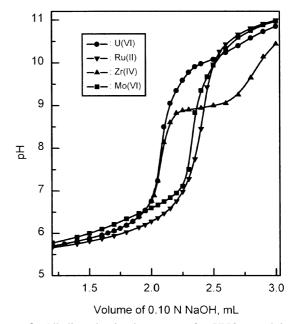

Figure 1. Alkalimetric titration curves for HNO_3-metal ion in noncomplexing medium; HNO_3: 0.202 meq, metal ion: 0.02 mmole.

thanide ions also hydrolyze slightly. Although the chemistry of molybdenum and ruthenium in aqueous solution is ambiguous, evidences for their hydrolysis have been reported.[23]

Each titration curve shown in Figure 1 was obtained in the noncomplexing medium containing 0.202 meq of nitric acid and 5.0 x 10^{-4} M of one metal ion of U(VI), Nd(III), Ce(III), Zr(IV), Mo(VI) and Ru(II) using the titrant of 0.10 N NaOH. In spite of the same titration condition, the titration curves differed from each other in shape and position due to the different hydrolysis properties of metal ions. Two sharp pH breaks, of which the first (pH 5.5) is responsible for the neutralization of free acid and the second (pH 9.5) for the hydrolysis of Nd(III) ion, were distinct for Nd(III) ion with a low hydrolysis tendency. U(VI) ion with moderate hydrolysis properties showed one broad pH break (pH 4.2) corresponding to free acid and two clear breaks (pH 5.5 and 8) related to hydrolysis and polymerization. However, only one pH break appeared for Zr(IV) ion which has a significant hydrolysis tendency, since nitric acid and hydrogen ion originated from the hydrolysis of Zr(IV) ion were simultaneously neutralized. The end-point for the nitric acid at a titrant volume of approximately 2 mL was well defined for Nd(III), and poorly for U(VI). But it could not be defined for Zr(IV) at all. Figure 1 showed that Ru(II) and Mo(VI) ions also hydrolyzed and interfered the titrimetric determination of free acid. The extent of hydrolysis of Ru(II) and Mo(VI) ions seemed similar to that of U(VI) ion as we compared the shape and position of the titration curve for U(VI) with those for two metal ions. It can be seen in Figure 1 that the titration curve for Ce(III) nearly overlapped with that for Nd(III) as expected from their hydrolysis constants. In all cases except for Nd(III) and Ce(III), the sharp pH break stemmed from

Figure 3. Alkalimetric titration curves for HNO$_3$-metal ion in mixed 0.10 M potassium oxalate-0.10 M potassium fluoride complexing medium; HNO$_3$: 0.202 meq, metal ion: 0.02 mmole.

the hydrolysis of the metal ion could be misinterpreted as the end-point for the neutralization of free acid by a visual inspection or a derivative method since the end-point for the neutralization of free acid was indistinct.

Figure 2 and 3 showed the titration curves obtained by using the oxalate or the mixed oxalate-fluoride medium instead of the same volume of deionized water in Figure 1, respectively. The titration in the presence of Nd(III) and Ce(III) was not studied further since it was confirmed that they do not significantly hydrolyze even in the absence of complexing agents. It is well known that Zr(IV) forms such stable complexes with oxalate and fluoride that can effectively repress the hydrolysis of Zr(IV) ions.[24,25] The titration curve for Zr(IV) at around pH 8.8 in Figure 2 was horizontal, indicating that oxalate complex of zirconium does not hydrolyze at the end-point. Hence, in the case of Zr(IV), the inflection points of the sharp pH breaks in Figure 2 and 3 were in good agreement with the amount of nitric acid present in the solution. As we can expect from the fact that uranium(VI) forms the mixed oxalatofluoride complex which is highly stable against hydrolysis,[26] Figure 3 showed a good titration curve in the mixed oxalate-fluoride medium containing U(VI) ions. Whereas, in cases of Ru(II) and Mo(VI), no advantages in terms of displaying a correct end-point were found by substituting the noncomplexing medium with the oxalate or the mixed oxalate-fluoride medium. It thus appeared that oxalate and fluoride do not effectively prevent the hydrolysis of molybdate and ruthenium nitrosyl adducts during the titration, although the formation of molybdate complexes of oxalate and fluoride and ruthenium nitrosyl complexes of oxalate were reported.[24,27] These results indicated that none of the three media could be used as a titration medium for the samples containing

Figure 2. Alkalimetric titration curves for HNO$_3$-metal ion in 0.20 M potassium oxalate complexing medium; HNO$_3$: 0.202 meq, metal ion: 0.02 mmole.

Mo(VI) or Ru(II) of above 0.02 mmole provided that a visual or a derivative method was employed to determine the end-point of titration. This amount of Mo(VI) or Ru(II) was approximately equivalent to that present in the spent fuel containing about 500 mg of uranium. On the other hand, 0.02 mmole of Zr(IV) would not hinder the titrimetric determination of free acid by such two complexing methods even though a simple visual way or a derivative method was used for the estimation of the end-point.

Effect of uranium concentration on titration curve. Since uranium is the major constituent of spent fuels, the extent to which U(VI) ion affects the titration is of great importance for the accurate determination of free acid in spent fuel solutions. The use of noncomplexing medium for the titration of free acid has not been generally favoured since it is known to give highly positively biased results at higher concentrations of the hydrolyzable metal ions in samples.[8] However, the noncomplexing method is simple and has advantages over the complexing methods in terms of the treatment of radioactive wastes resulted from the titrations. Thus, the present study is intended to evaluate the feasibility of the noncomplexing medium for the titration of free acid in the concentrated uranium solutions with high molar ratios of U(VI)/H$^+$. As can be seen from Figure 1, the end-point for the free acid could not be accurately determined by using the noncomplexing method and a visual or a derivative method due to indistinct inflection at 5 mg of uranium concentration and U(VI)/H$^+$ molar ratio of 0.1. This problem became worse with increasing the uranium concentration.

The titrations of 0.4126 meq of nitric acid in the noncomplexing medium were carried out, with various uranium concentrations of 60, 120, 300, and 400 mg. The inflection point
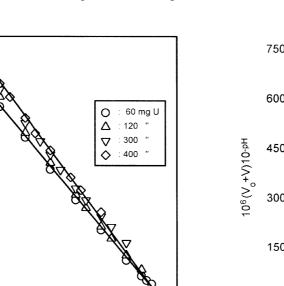

Figure 5. Effect of uranium concentration on Gran plot for the alkalimetric titration of free acid in the 0.20 M potassium oxalate medium; HNO$_3$: 0.4126 meq.

on the titration curves became obscure with increasing uranium concentration. The titration curves obtained in oxalate medium for the same uranium solutions were also similar to those in noncomplexing medium, and the inflection point could not be determined by a visual inspection or a derivative method in the presence of a low concentration of uranium around 60 mg. These results indicate that uranium oxalate complexes easily hydrolyze with increasing pH. On the other hand, in the case of the mixed oxalate-fluoride
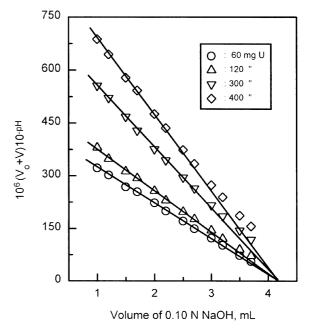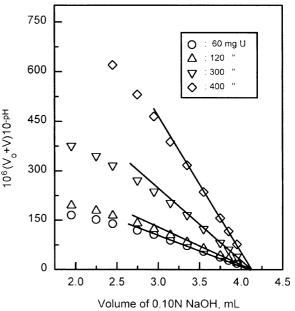

Figure 4. Effect of uranium concentration on Gran plot for the alkalimetric titration of free acid in noncomplexing medium; HNO$_3$: 0.4126 meq.

Figure 6. Effect of uranium concentration on Gran plot for the alkalimetric titration of free acid in the mixed 0.10 M potassium oxalate-0.10 M potassium fluoride medium; HNO$_3$: 0.4126 meq.

medium, one sharp pH break appeared and its inflection point was in good agreement with the theoretical end-point of nitric acid present in the medium containing a large amount of uranium about 500 mg.

Determination of end-point by Gran plot. Figure 4 explained how the end-point could be determined by extrapolation of the linear portion in the Gran plots for the titrations of the free acid in the noncomplexing medium containing uranium. The Gran plot method for the titrations shown in Figure 5 and 6 was also used for oxalate and oxalate-fluoride media containing relatively high concentrations of uranium mentioned in the previous section, respectively. The points represented with symbols according to the Gran plot method indicate the amounts of hydrogen ion remained in the titrated solutions. V_o is the initial volume of the titrated solution, V is the volume of the titrant added, and 1000 is arbitary constant as a convenience of plotting. In the noncomplexing and the oxalate media, Gran plot was linear at the early part of the titration, but became curved near the end-point of the titration due to the hydrolysis of U(VI) ion and uranium oxalate complexes. On the contrary, in the mixed oxalate-fluoride medium (Figure 6), a curvilinear relationship at the early part of the titration was followed by a straight-line relationship at the latter part of the titration. The linearity near the end-point indicates that fluoride complexes of uranium and oxalatofluoride complexes of uranium do not hydrolyze at the end-point.[8,26] The reason for the non-linearity of the plot in the early part of the titration seems to be due to the lack of response of the glass electrode in hydrofluoric acid.[8] As can be seen in Figure 4 and 5, the higher uranium concentration means the lower pH, where the non-linearity of the plot began. From the results of three methods, it can be seen that the extrapolated lines had the intercepts of the abscissa which were in good agreement with the theoretical end-point value of 4.126 mL.

Effect of the concentration of U(VI) in titration media on the recovery of nitric acid was also examined to determine the upper limit of U(VI)/H$^+$ molar ratio. Results of the five replicate titrations in the noncomplexing medium were shown in Table 2 together with the results obtained in the two complexing media for comparison. The free acidity determined by the three methods agreed well with true values at U(VI)/H$^+$ molar ratio of up to about 5. The accuracy and precision of the noncomplexing method were found to be comparable to those of the two complexing methods. The biases of results in the noncomplexing medium were less than ±1% and about +3% respectively for 0.4 meq and 0.05 meq of free acid at the U(VI)/H$^+$ molar ratio of up to about 5. The relative standard deviations of results ranged from 0.5 to around 6%. The noncomplexing method gave very reliable results irrespective of uranium concentrations studied. However, the linear portion of Gran plot became much narrower with increasing the molar ratio of U(VI)/H$^+$, and the upper limit was found to be about 5.

In addition, Table 2 indicated that the positive bias increased with decreasing the concentration of nitric acid up to 0.05 meq at the U(VI)/H$^+$ molar ratio of about 5, in spite of the
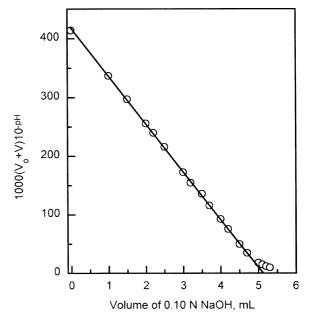
Table 2. Determination of free acid at various U(VI)/H$^+$ molar ratios by the three methods and the Gran plot end-point prediction technique

Amount taken			HNO$_3$ found, meq			
U, mg	HNO$_3$, meq	U/H$^+$ ratio	noncomplexing method		oxalate method	oxalate-fluoride method
			bias, %	RSD, %		
60	0.4126	0.6	0.413 +0.2	0.6	0.413	0.413
120	0.4126	1.2	0.412 -0.3	0.5	0.412	0.413
300	0.4126	3	0.412 -0.2	0.8	0.412	0.413
400	0.4126	4	0.414 +0.4	1.0	0.413	0.414
500	0.4126	5	0.412 -0.3	1.0	0.414	0.413
120	0.1093	4.6	0.109 -0.5	2.7	0.119	0.109
60	0.0546	4.6	0.056 +2.9	5.8	0.068	0.053

low concentration of U(VI), particularly in the noncomplexing and the oxalate media. On the other hand, the oxalate-fluoride method gave a good result even at the nitric acid concentration of 0.05 meq. Thus the nitric acid concentration of 0.05 meq would be close to the lower limit for which the end-point could be precisely located by the Gran plot.

Determination of free acid in simulated spent fuel solutions. Since Zr(VI) ion has been well known as one of the most hydrolyzable metal ions, we considered Zr(VI) ion as a representative in the titration of spent fuel solutions. When we employ the Gran plot technique for the determination of end-point, the Zr(IV) ions, even up to 250 times those present in the spent fuel solution with 2 mg U, did not interfere during the titration of 0.4126 meq HNO$_3$ in the three titration media. We could thus expect that the total amount

Figure 7. Gran plot for the alkalimetric titration of free acid in a simulated spent fuel solution by the noncomplexing method; HNO$_3$: 0.5034 meq, U: 50 mg, Cs: 125 μg, Ce: 125 μg, Mo: 176 μg, Nd: 213 μg, Ru: 117 μg, Zr: 190 μg.

of the fission product metals present in the spent fuel containing 2 mg of uranium might not cause problems in the similar titrations. Titrations of free acid were conducted in the solutions containing 0.5 meq of nitric acid, 2 or 50 mg of U(VI), and the amounts of major fission product metals calculated on the basis of the uranium contents. The results obtained from the three titration media were in good agreement with the theoretical value of 0.5 meq HNO_3. Figure 7 presented a Gran plot for the titration carried out in the noncomplexing medium containing 0.5034 meq of HNO_3, 50 mg of U(VI) as well as several hundred micrograms of the major fission product metal ions.

Aliquots of 50 μL of the spent fuel solution were analyzed for the free acid concentration by the three methods. The uranium concentration of this solution was found to be 10.30 mg/mL by the Davies-Gray method. Thus, the amount of uranium contained in 50 μL of sample was about 0.5 mg and the total amount of major fission product metal elements was negligible. Duplicate titrations of the free acid in the spent fuel solution with the 0.10 N NaOH titrant were conducted by the three methods, and the end-point was determined by the Gran plot. As expected from the fact that the small amounts of uranium and fission product elements were contained in the sample, the Gran plots obtained from the noncomplexing and the oxalate media showed linearity from the beginning of titration to the end-point of the free acid as if the sample was a pure nitric acid solution. The Gran plot for the mixed oxalate-fluoride medium was curved in the early part of the titration but became linear towards the end-point. The nitric acid concentration determined by the noncomplexing method was in good agreement with those obtained by the two complexing methods, and the average normality value of nitric acid was 7.699 for the noncomplexing method, 7.707 for the oxalate one, and 7.697 for the mixed oxalate-fluoride one.

Conclusions

We investigated the performance of noncomplexing-Gran plot titration method together with two complexing methods in order to apply the noncomplexing method to the determination of free acid in highly radioactive spent fuel solutions.

Zr(IV) ion severely interfered in the free acid titration by noncomplexing method, Ru(II) and Mo(VI) ions appeared to do moderately like U(VI), and Cs(I), Ce(III) and Nd(III) ions nearly did not, and the magnitude of their interferences in titration parallels their hydrolysis tendencies. The experimental results showed that the noncomplexing method using the Gran plot end-point prediction technique allowed the titration of free acid in the presence of relatively large quantities of these metal ions. The results obtained by the noncomplexing-Gran plot titration of free acid in several solutions containing uranium and nitric acid in a wide range of U(VI)/H$^+$ molar matios agreed well with those obtained by two complexing methods. The accuracy and precision of the noncomplexing method were found to be much high for

the moderate free acid concentrations at the various U(VI)/H$^+$ molar ratios up to 5, and comparable to those for the two complexing methods. However, at such a low free acid concentration as 0.05 meq, the noncomplexing method provided somewhat less accurate results than those from the mixed oxalate-fluoride method, but more accurate results than those from the oxalate method. This study confirmed that the noncomplexing-Gran plot titration method was applicable to very small aliquots of samples (less than 100 μL), which made it useful especially for highly radioactive solutions.

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