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Review

Free acidity measurement – A review

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ABSTRACT

Free acidity is an important parameter especially in the presence of hydrolysable ions. Several methods have been developed for the determination of free acidity, attributing due importance to the accuracy and the precision of the measurement with the aim of the easiness of the methodology as well as post-measurement recovery in mind. This review covers important methods for the determination of free acidity with emphasis on actinide containing solutions, reported in the literature over the past several decades classifying them into different categories.

Contents

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1. Introduction

Free acidity of a solution containing hydrolysable metal ions is defined as the acidity in excess of the stoichiometrically balanced salts or the acidity without taking into account that contributed by the hydrolysis of such metal ions. It can also be simply defined as the acidity of the solution when the hydrolysable metal ions are removed or complexed so as not to interfere during the measurement. The term “free acidity” is used always to quantify the acidity of solutions containing hydrolysable ions such as UO_2^{2+}, U^{4+}, Pu^{4+}, Th^{4+}, Zr^{4+}, trivalent lanthanides, actinides, transition metal ions such as Al^{3+}, Fe^{3+}, Cr^{3+}, Co^{3+}. It should be noted that anions such as phosphate, acetate, and oxalate and cations such as ammonium ion present in the solution also can interfere in free acidity measurement through buffering action during alkalimetric titrations.

Typical chemical engineering operations such as spent fuel reprocessing involving the separation and recovery of highly hydrolysable actinide ions Pu(IV) and U(VI) employing the PUREX process [1,2] demand free acidity measurements during dissolver solution conditioning, process control analyses, partitioning of Pu and U, stripping steps and also during the final reconversion steps. Waste management operations [3], which follow the spent fuel reprocessing operations, involve neutralization, precipitation, solvent extraction, ion-exchange, etc., wherein free acidity measurements are essential. Studies on polymerization, hydrolysis and complexation involving hydrolysable ions also necessitate free acidity measurement. The measurement is carried out using alkalimetric titration after the removal of the hydrolysable ion by a suitable method such as ion exchange, precipitation or solvent extraction or suppression by complexing the metal ions. The free acidity measurement becomes increasingly inaccurate when the ratio of the concentrations of the hydrolysable metal ion to the acid increases. The difficulty in the preparation of standard solutions with known free acidity makes the assessment of a particular method with respect to the accuracy or the choice of a suitable complexant difficult.

The literature on measurement of free acidity dates back to 1890 [4] or earlier, wherein measurement of free acid in the presence of aluminum salts have been discussed. The present review gives an overview of the literature reported methods for the determination of free acidity, describing the techniques used for the suppression of hydrolysis as well as for the measurement of the acidity. This review also describes methods developed to simultaneously measure the concentrations of hydrolysable metal ions and other additives such as hydrazine, in addition to the free acidity. Importance has been given to free acidity measurement in the presence of actinides.

The suppression methodologies adopted for overcoming the influence of the hydrolysable metal ions and subsequent free acidity measurement techniques developed are listed below. There are further choices in the use of titrants, which can be NaOH, Na_2CO_3 or alkali generated electrochemically. Also several non-aqueous titrations involving non-aqueous titrants such as cyclohexylamine and pyridine have been used. All the methods have attempted in addition to getting good accuracy and precision, simplification of the procedure, reduction of the corrosion problems of the waste generated, making the recovery of the hydrolysable ions such as actinides which are both valuable and radiotoxic, easier and ensuring long life for the detection equipment such as pH measuring electrodes.

Usually the metal salts are purified by recrystallization from saturated solutions in high purity water under near neutral pH conditions and do not contain any associated acid. For highly hydrolysable metal ions such as Pu(IV), U(IV), U(VI) and Th(IV) getting near neutral salts without accompanying acid is very difficult which in turn makes getting “free acidity standards” through this route nearly impossible. This monograph also describes some of the methods used for the preparation of “free acidity standards” though their reportings are scarce in the literature.

- Suppression techniques
  - Precipitation
    - iodate, ferrocyanide, peroxide
  - Complexation
    - Sulfate, oxalate, fluoride, oxalate–fluoride, thiocyanate, citrate, tartrate, EDTA, DTPA, TTHA
  - Addition of a neutral salt and titration in non-aqueous media
  - Removal by cation-exchange
  - Removal by solvent extraction
- Measurement techniques
  - Measurement of pH
  - Alkalimetric titration with pH measurement
  - Alkalimetric titration with visual indicators
  - Alkalimetric titration using constant current coulometry
  - Alkalimetric titration using conductometry
  - Alkalimetric high frequency titrations
  - Alkalimetric titration using thermometry
  - Gran titration with alkali
  - Potentiometry with standard addition of acid
  - Non-aqueous titrations

2. Hydrolysis suppression by precipitation

Hexacyanoferrate ($Fe(CN)_6^{4-}$) has been employed for the precipitation of uranium [5,6] for the free acidity determination. The method for uranium however required addition of methanol for preventing the uranyl hexacyanoferrate complex from dissociation and the dark color precipitate prevented subsequent visual indicator based titrations. The recovery of uranium from the waste was also found to be difficult. Ferrocyanide precipitation method is not applicable for Al(III) containing solutions.

KIO_3 has been used to precipitate and remove Pu(IV) in free acidity determinations and has been reported to give a slight negative bias possibly due to the acid-iodate formation. Dahlby et al. [7] investigated this method in detail in comparison with sodium citrate complexant. They prepared “free acidity” standards by (1) dissolving high purity plutonium metal in HCl while trapping the evolved acid, (2) dissolving PuO_2 in HCl at high temperature in a sealed tube and (3) dissolving dicesium plutonium hexachloride (Cs_2PuCl_6) in prestandardised HCl. While the iodate method involved the use 0.3 M KIO_3 for precipitation of acid solution containing not more than 50 mg Pu(IV), filtering the precipitate and washing the precipitate with same iodate and titrating the filtrate and washes with 0.3–0.4 M NaOH to point of inflection. In the citrate procedure a sample aliquot containing not more than 25 mg Pu is added to 30 mL of 10% sodium citrate (whose pH is known), and titrated with sodium hydroxide to same pH. Comparison of the results indicated that the citrate complexation method reported positive bias to the extent of 6–9% while the iodate method gave better than 99% recovery with bias $\leq 1\%$. Pu (III) was found to interfere in both iodate and citrate methods by yielding negative (94–96% recovery) and positive (+9%) biased results, respectively. The negative error in iodate was attributed to the oxidation of Pu(III) to Pu(IV) by iodic acid. In the free acidity measurements of Ce (III) solutions, both these methods gave bias free results due to the absence of oxidation, while both the methods yielded positively biased results with Ce(IV) solutions. Ammonium ion was found to interfere due to buffering action in the iodate method and even more in citrate method.

Determination of the free acidity in Th(IV) standard solutions prepared by sealed tube dissolution of ThO_2 in HCl also indicated a positive bias of 9% in the case of citrate method while iodate method was bias free.

Smith [8] determined the free acidity using iodate precipitation from nitrate, chloride, sulfate and perchlorate solutions of Pu(III), Pu (IV) and Pu(VI) with good precision(std. deviation of ~0.9%). Citrate and tartrate were found to interfere in anion to Pu mole ratios above 5. The procedure involved precipitation of Pu with iodate and titrating the filtrate with sodium hydroxide to inflection point. Phenolphthalein could be used in the absence of Pu(VI) to detect the endpoint. The method also provided measurement of Pu(VI) using the amount of base consumed in the buffering region between the two inflection points of the potentiometric titration curve.

Baehr and Thiele [9] reported a method for the determination of free acid and U(VI) in the presence of high Pu(IV) concentration after separating Pu(IV) with HIO_3 as $Pu(IO_3)_4$. The method could also be applied to organic solutions of Pu(IV), U(VI), and H^+.

The same authors also reported [10] the determination of free acid in nitric acid solutions of Pu(IV) (up to 0.5 M), wherein Pu(IV) is reduced to Pu(III) with mercury and the acidimetric titration without any separation. U(VI) could be tolerated up to a ratio of 10:1(U(VI):Pu(IV)). The method was found to erratic in the presence of large Pu(VI). The relative standard deviation (RSD) obtained was in the range from ±0.4 to ±1%.

Vogg [11] reported a potentiometric method for the free acid and Pu determination in nitric acid solutions.

2.1. Hydrolysis suppression by complexation

2.1.1. Sulfate

Ahrland [12] developed two methods for the determination of free acidity in the presence of large amount of uranyl salts, the first by complexing uranyl ions by sulfate and titrating the acid with standard alkali and the second for determining small concentrations too low for titration, by measuring the pH in the presence of complexant. He used ammonium sulfate as the complexant in both the methods.

Chwastowska and Skwara [13] potentiometrically determined free acid in the presence of uranyl, aluminum, and magnesium nitrates. Samples of 0.2, 1.0, or 2.0 mL of 0.1–8.0 M HNO_3 containing 50–400 mg U/mL were potentiometrically titrated with 0.1–0.4 M NaOH in the presence of $(NH_4)_2SO_4$. The relative error of the estimation grew larger as HNO_3 content decreased in the sample and was 0–8.0%. Mg at 2–50 mg/mL, did not interfere, but at 2–150 mg Al/mL, the error increased with Al concentration. An addn. of 25% potassium oxalate in amounts three to ten times that of Al, on the molar basis, suppressed the Al interference.

Motojima and Izawa [14] described a simple method for the determination of free acid and U(VI) in U solutions using alkalimetry after masking U(VI) with $(NH_4)_2SO_4$. After the equivalence point, H_2O_2 is added to the solution and the liberated acid equivalent to U is titrated with the same alkali solution. Around 25 mg to 2 g of U(VI) and 0.05–30 meq. of HNO_3 could be readily determined. The method could also be applied for the determination of HCl, or H_2SO_4 and U(VI) and for the determination of U(VI) in tributyl phosphate/kerosene solutions.

2.1.2. EDTA

The use of EDTA to overcome metal ion interference in the determination of the acidity of aqueous solutions has been reported [15,16]. In the first method reported by Fatu [15], sufficient EDTA is added to complex all of the Zn and iron (Fe) ions present. The titer obtained in the determination of the acidity of this solution is then corrected for the acid liberated during the formation of the Fe-EDTA and Zn-EDTA complexes. In the second reported by Tomasevic [16] method Ca-EDTA supplies the EDTA to complex interfering metals in titration to pH-4. The use of this reagent for titrations to pH-8 may lead to error because calcium carbonate ($CaCO_3$) is more likely to be only partially neutralized.

2.1.3. DTPA and TTHA

Nakashima and Lieser [17] utilized the complexing agents diethylenetriaminepentaacetic acid (DTPA) and triethyleneteraminehexaacetic acid (TTHA) for the free acidity determination in solutions containing U(VI), Th(IV), U(IV), Zr(IV) and U(VI)–U(IV), U(VI)–Th(IV) mixtures, for essentially avoiding the interference caused by precipitation of tetravalent ions in the oxalate–fluoride procedure. The procedure involved use of 0.2 M DTPA solution of pH 6.1–6.86 or 0.2 M TTHA of pH 7.8 to complex the metal ions and titrating with NaOH to get the total acidity which is contributed by both free acidity and that due to the acidity from complexation reaction. When DTPA used alone as the complexant resulted in the following bias for the maximum permissible amount of hydrolysable ion indicated in parenthesis. For Th(IV), ±1.4% (116 mg), for U(IV), ±2.0%(245 mg), for Zr(IV), ±2.3% (46 mg). In U(VI)–U(IV) mixtures the combination of DTPA and oxalate/fluoride (2:1) permitted 119 mg U(VI)–209 mg U(IV) with ±3.9% bias whereas in a U(VI)–Th(IV) mixture of 119 mg U(VI)–464 mg Th(IV) reported a bias of ±2.7%. The authors have not provided any information on the precision.

2.1.4. Oxalate

Oxalate complexation and alkalimetric titration has been one of the oldest and most used methods for routine free acidity determination in many PUREX plants for the process stream samples [5,18,19] from early 1950s. The advantages of this method are that the recovery of the metal ions, especially the actinides, is very easy as the oxalate is easily destroyable and also the oxalate forms soluble complexes with most of the hydrolysable ions such as Al(III), Pu(III), Pu(IV), U(IV) and Th(IV) making the estimation procedure simple. Ammonium, sodium and largely potassium oxalates have been used for complexation. Nevertheless the validity of the method for high $[M]/[H^+]$ ratios has been always questioned and many have attempted to address this.

Pakalns [20] studied in detail the oxalate complexation (using saturated potassium oxalate solution) for the determination of free acidity in the presence of the hydrolysable ions using two methodologies. Bi(III), Ce(IV), Sb(III), U(VI) and V(V) were determined by titrating with sodium hydroxide to the inflection point with potassium oxalate or to preadjusted pH of 6.05 with sodium oxalate. Phosphate was found to interfere. Al(III), Hg(II), Fe(III), V (VII) and Zr(IV) were determined by finding out the point of intersection of the titration curve which exhibited a break after the steep rise. Ti(IV) was found to interfere severely as it did not form a strong oxalate complex. Ammonium ions were found to interfere and the interference of more than 1 mmol ammonium ion could be overcome by the addition of extra potassium oxalate for complexation. Solutions containing cations such as Cr(III) which form complexes very slowly with oxalate were boiled with oxalate and cooled before titration.

2.1.5. *Oxalate and fluoride*

Mayankutty et al. [21] made two modifications in the existing method of determining the free acidity by alkalimetric titration in neutral potassium oxalate medium [18] to improve the reliability of determination, for solutions containing high concentrations of uranium. They also compared the results of the methods with those obtained by cation exchange method. The first modification utilized the principle that when uranium is titrated with NaOH in the presence of oxalate to pH 9, the total alkali consumed is due to the free acidity and uranium. The second method utilized complexation with an oxalate–fluoride mixture (typically 25 cm^3 of 10% potassium oxalate with 1–3 cm^3 of 1 M NaF preadjusted to pH 7) and titration to pH 7 with alkali. The third method consisted of alkalimetric titration of an aliquot of the sample in 10% potassium oxalate as described in the previous method but without the addition of fluoride. They compared the results using the cation exchange method [22] which used a resin bed of 8 mm(id) × 100 mm(h) of DOWEX 50 × 8 (50–100 mesh) in H^+ form through which the sample was passed to get the total acidity which if subtracted for uranium contribution will give free acidity. They also explored the tolerance limits for all the three procedures for the ions Th(IV), Al(III) and Fe(III) and found the oxalate–fluoride method to be superior with respect to accuracy, precision and tolerance of impurities.

Benadict et al. [23,24] reported that in their attempt to measure the distribution ratios of U(VI) from nitric acid medium during the extraction by 1.1 M tri-isoamyl phosphate/*n*-dodecane under high loading conditions, free acidity measurements in the organic phase using oxalate–fluoride mixture as complexant yielded more reliable results than oxalate alone. The mole ratio of metal:free acid in such measurements was 10:1.

Solomons [25] examined seven methods for the titrimetric determination of free acid in the presence of hydrolysable cations with primary aim of the free acidity determination in solutions resulting from leaching of Au and U ores with H_2SO_4. The effects of the individual cations Fe(II), Fe(III), Al, and Mn(II) at concentrations of ~2 and 10 g/L on solutions containing H_2SO_4 at concentrations of ~0. 6, 1, and 3 g/L were studied. The pH values of the solutions were plotted against the corresponding vols. of titrant for five of the methods that involved titration with an alkali. This procedure was also used for a solution containing a mixture of the above cations and Ca at concentrations similar to those of U-plant leach liquors, for two production-plant U leach liquors, and for liquors derived from the leaching of Cu–Zn ores. The method based on the formation of complexes between the cations and $K_2C_2O_4$ had the fewest defects. Methods based on the formation of complexes with fluoride, the enhancement of H^+ activity by concentrated LiCl, the removal of salts of hydrolysable cations by their precipitation with acetone, and the reduction of Fe(III) by KI failed either in the presence of individual hydrolysable cations or in the presence of mixtures of these cations. Relative std. deviations (in 6 determinations) for the solution containing a mixture of cations and 6.5 g H_2SO_4/L ranged from 0.0066 to 0.023. Solutions containing Fe(II) yielded low and erratic results owing to their oxidation by air and the accompanying abstraction of H ions. This has important implications with respect to the sampling and storage of such solutions.

2.1.6. *Fluoride*

Menis et al. [26] used an automatic Sargent-Malmstadt differential titrator to determine the free acidity of uranyl sulfate solutions using fluoride as complexant. The [U]/[H^+] ratio in their study varied from 0.5 to 16 with precision (RSD) achieved ranging from ±1.5% to ±3.0%, respectively. The advantage of using this titrator is that instead of the glass electrode which gets degraded by the fluoride used as the complexant, platinum or platinum–10% rhodium was used as the pH indicating electrode in combination with saturated calomel reference electrode.

Scargill et al. [27] determined the free acidity of UO_2^{2+} by titration with NaOH after complexing with F^- to prevent hydrolysis using a computer controlled autotitration routine as well as the Gran plot technique for prediction of the end-point. The titration errors were quantitatively identified and used in the correction of titer values obtained in the presence of U. The precision was equiv. to ±0. 002 meq of H^+ for the titration of ~0.4 mmol HNO_3. Using a differential acidity technique, with corrections made for the errors introduced by the quantities of free acid and U present, the accuracy of determination was ~ ±7% to ±2%, respectively for 0. 05 meq to 0. 2 meq of free acid in the presence of up to at least 2 mmol U.

Crossley [28] compared the performance of a direct titration method and an indirect mass balance method for the determination of free acid in highly concentrated solutions of uranyl nitrate and Pu nitrate was compared. While the direct titration of free acid with alkali is carried out in a F^- medium to avoid interference from the hydrolysis of U or Pu, the free acid determination by the mass balance method is derived from the metal concentration, metal valency state, and total nitrate concentration in the sample. The use of the Gran plot technique was seen to improve the detection of the end-point of the free acid titration. The results of both the methods agreed well. The error of the direct titration method in F^- medium using the Gran plot technique to detect the end-point was ±0.75%.

Schmid and Juenger [29] reported a fluoride suppressed method to determine the free acidity of U(IV) using potentiometric titration with 0. 1 N NaOH and compared the results with those obtained by other methods. In the presence of <30 mg U(IV), no systematic errors were observed. Negative errors caused by 30–260 mg U(IV) were corrected by calculation. The relative std. deviation for 0.4 and 2 mmol acid in the presence of 26 and 130 mg U(IV) was 1.4% and 0.26%, respectively (12 determinations). The U(VI) content of the sample was determined by continuing the titration until a 2nd maximum appeared. Al(III) (<3 mg) and Fe(III) (<25 mg) did not cause any interference.

2.1.7. *Citrate*

Bishop and Summ [30] reported a procedure for the free acid determination in descaling solutions containing ferric ions. The method involved using saturated sodium or potassium citrate complexed solution and titrating with NaOH to phenolphthalein end-point. Maintenance of citrate concentration in near saturated condition near the end point was essential to get good precision. Pflug and Miner [31] assessed the measurement of free acidity of plutonium solutions using various complexants such as sodium citrate, potassium oxalate and potassium citrate by alkalimetric titration with NaOH using a precision Dow automatic titrator. A detailed comparison between oxalate and citrate indicated that citrate is a better complexant for plutonium if the starting and end point pH are between 7.5 and 8.5 (with bias <0.1 N). They also reported that the iodate method [8] gave lower free acidity values possibly due to the formation of acid-iodate precipitates.

2.1.8. Tartrate

Soundar Rajan [32] reported a method for free acidity determination in Sb(III) chloride solutions with tartrate as complexant. While the total acidity is measured with tartrate as masking agent, the bound acidity is derived from the antimony content determined by titration with bromated.

2.1.9. Thiocyanate

Baumann et al. [33,34] reported an unique standard addition method for the determination of free acidity in solutions containing Al(III), Cr(III), Fe(III), Hg(II), Ni(II), Th(IV) and U(VI). The method used 1 M potassium thiocyanate as the complexant to which sample aliquot containing around 10 μmol acid is added followed by two incremental additions of known acid and measuring the potential of the solution using a glass combination electrode with a pH meter. The free acidity was evaluated by solving three simultaneous equations or by Gran procedure or employing a microprocessor based pH meter. The advantage of the method is that it totally minimizes the hydrolysis by avoiding higher pH conditions while making the free acidity measurements unlike the normal alkalimetric titrations. The complexant provided additional control over the hydrolysis and potassium thiocyanate was chosen as it is a moderately strong complexing agent for most of the metal ions and is the salt of a strong acid and strong base and does not exhibit any buffering action. The method is applicable to $[M]/[H^+]$ ratios of <2.5. The accuracy of the method could be judged from the Nernst slope found in the presence and absence of hydrolysable ions and the relative standard deviation was $<2.5\%$.

3. Measurement techniques

The following sections describe the measurement techniques employed for the determination of free acidity with or without using suppression techniques.

3.1. Measurement of pH

The method developed by Ahrland [12] to determine the free acidity after complexation with sulfate and measuring the pH has been discussed earlier. Lu Zhi-Ren et al. [35] modified Ahrland's procedure taking into account the acidity of the saturated ammonium sulfate solution to which known aliquots of solution whose free acidity to be determined are added. Using this method they could achieve better accuracy and precision for the free acidity measurement of solutions containing $[\text{uranium}]/[H^+]$ mole ratios ranging from 2 to 8 with relative standard deviation of $<3\%$. It should be noted that the pH measurement method is applicable to solutions containing only one hydrolysable ion.

Jones et al. [36] developed a direct pH measurement method for the determination of free acidity in solutions containing aluminum (III), thorium (IV) and uranium (VI) ions. The method is applicable to solutions with $[M]/[H^+]$ ratios exceeding 20 where the traditional complexation for masking the hydrolysable ion fails and is valid for solutions where the free acidity or acid deficiency is not greater than 0.1 M. The method gave errors of magnitude ± 0.03 M for error in pH measurement of 0.05 units and temperature variation was found to affect the measurements insignificantly.

3.2. Solvent extraction and alkalimetric titration

Marshall and Bar-Nun [37] developed a procedure to determine the free acidity in solutions containing uranyl nitrate (0.1–1.5 mmol of acid in the presence of 1 mmol of uranium), which involved potentiometric titration to pH 3.4, after solvent extraction of uranium by neat TBP using saturated KCl or KNO_3 as the salting agent to aid the extraction of uranium. They reported a precision of $\pm 4.2\%$ for $[U]/[H^+]$ mole ratio of ~ 5 and $\pm 0.3\%$ for a ratio of 0.65.

3.3. Cation exchange and alkalimetric titration

Dizdar and Obrenovic [38] developed an ion-exchange method for the determination of free acid in solutions containing uranium (VI). The solution containing U(VI) is passed through a cation exchanger in the hydrogen form and the effluent is titrated with alkali to determine the total acidity. With the knowledge of the uranium content of the original solution, the free acid can be calculated. The procedure was tested for solutions with $[\text{uranium}]/[H^+]$ ratios raging from 1:25 to 52:1 with acid concentration ranging from 0.02 to 7.6 N.

This method is also applicable to solutions containing other hydrolysable cations. Though considered to be an accurate, this method suffers the following disadvantages: (1) the cationic content and valency should be accurately known, this makes the procedure not suitable for free acidity measurement in nuclear reprocessing streams where a large number of metal ions are likely to be present, (2) for large $[\text{Metal}]/[H^+]$ ratio the error in acidity determination will be seriously affected by error in the estimation of the concentration of the cation, (3) the procedure is tedious, (4) the aliquot size and cation exchange resin amount have to suitably chosen so as to avoid breakthrough of the metal into the effluent.

Campbell [39] reported a cation exchange separation followed by alkalimetric titration for the determination of the free acidity.

Perez Bustamante [40] observed an anomalous ion-exchange behavior of stoichiometric acid free freshly prepared and strongly aged (7–8 years) uranyl nitrate solutions. While the freshly prepared solutions undergo completely normal stoichiometric anionic and cationic exchange when percolated through strongly acidic or basic ion-exchange resins, the aged solutions show a strikingly anomalous cation-exchange behavior since the uranyl cation exhibits an apparent net electrical charge of about 4+. On the basis of these findings it is concluded that proper attention should be paid to possible restrictions in the applicability of cation-exchange resins for the determination of free acidity in uranyl nitrate solutions, especially when dealing with aged solutions of very low free acidity.

Gaddy and Dorsset [41] reported an automated ion exchange followed by colorimetry using thymol blue indicator for the determination of free acidity in hydrochloric and nitric acid solutions of La^{3+}, Al^{3+},Th^{4+} and $UO_2{}^{2+}$.

3.4. Alkalimetric titration using conductometry

Booman et al. [42,43] developed conditions for getting minimum bias during the determination of free acidity employing oxalate complexation and alkalimetric titration. They used conductometry for the estimation of the free acid in the solutions of hydrolysable ions as it is very difficult to get free acid standards.

Pepkowitz [44] determined free acidity in nitric and sulfuric acid medium in the presence of large amounts of Al(III) and stainless steel component metal ions by complexing with fluoride and conductometric titration. They found that the ratio of $[F^-]/[M]$ had to be kept within a narrow range to get stoichiometric recoveries of free acid and good end points. Propst [45] reported that there was no significant effect by changing the $[F^-]/[Al^{3+}]$ ratio from 2 to 3 again using conductometry.

3.5. Alkalimetric titration using constant current coulometry

Sreenivasan et al. [46] devised a constant current coulometric procedure for the determination of free acidity in uranyl nitrate containing nitric acid solutions using 1 M sodium sulfate as the complexing agent. The method was studied for [U]/[H^+] ratios varying from 0.15 to 1.6, thus covering entire range of PUREX process streams and reported accuracies better than +6% and precision better than ±2%. The procedure involved taking the sample in a beaker containing the working electrode (a coiled platinum wire cathode) immersed in a well stirred 1 M sodium sulfate preadjusted to pH 4, applying a constant current of 10 mA between the working and the counter electrodes to generate hydroxide ions, titrating till pH reaches 4 and then recording the coulombs consumed from the integrator. The method had the following advantages over the conventional autotitration,

- The generation of the hydroxide ions can be controlled suitably choosing the current to avoid local hydrolysis
- Requires very small samples of equal or less than 10 μeq of the acid
- Could be easily automated
- Avoids preparation and storage of standards
- Does not result in any waste due to the internal generation of the titrant, which is of high significance in the estimation of free acidity of radiotoxic ions.

However the method also has the disadvantages of not being usable in the presence of less electropositive metal ions such as Cu (II), Ag(I), which reduce prior to the generation of hydroxide ion and similarly ions which tend to oxidize at the anode in preference to the oxidation of water.

3.6. Gran titration with alkali

The Gran titration [47,48] is a mathematical technique for finding the end point of an acid-base titration. The Gran titration essentially linearizes the titration curve by means of a simple function:

$$F=(v+\mathrm{Vo})*10^{E/a}$$

where F=Gran Factor, v=volume of alkali added to the solution in the titration vessel, Vo=original volume of the sample containing the acid, E=EMF (millivolts) at v and a=slope of electrode (use 59 mV/pH unit). If the value of F is calculated far from the end point, it turns out to be linear when plotted as a function of the volume of alkali added (v). The reason for measuring mV instead of pH is that the voltmeter gives one extra digit when measuring mV thus improving the precision. The optimum range of millivolts for linearity is in the range of 220–240 mV.

3.6.1. Advantages of Gran's method

Simplicity of measurement: Potentiometric readings can be taken after regular increments in v throughout the whole titration; unlike differential plots of dE/dv or dpH/dv against v, Gran plots do not require large numbers of readings, corresponding to very small changes in v, in the region of the equivalence point.

Simplicity of calculation: The calculations are quick and easy. Computer programmes are available for plotting the graph and deriving the result.

Precision: The end points obtained by a linear Gran extrapolation are much more precise than those obtained by the differential method, especially if the titration curve is not symmetrical.

Versatility: The method may be used when only part of the pH range is accessible to measurement, e.g., when the acid contains metal ions which hydrolyze in the region pH∼2.5. It would be very difficult to determine the concentration of strong acid in a solution of this type by conventional methods. Gran's method has the further advantage that the presence of carbonate in the alkali can readily be detected. The method also finds applications in titrations of polybasic acids, redox and complex formation and precipitation titrations as discussed in Gran's original paper.

Gran titrations can be performed to determine the free acidity as one need not titrate to the end point where hydrolysis of the metal ions are likely to occur. Suh et al. [49] studied in detail non-complexed alkalimetric Gran titrations to estimate the free acidity in the presence of hydrolysable ions such as Ce(III), Nd(III), Mo(VI), Ru(II), Zr(IV) and U(VI). For [uranium]/[H^+] mole ratios up to five free acidities could be determined with biases less than ±1% and ±3% for free acid contents of 0.4 and 0.05 meq, respectively. The results were also compared with those measured using complexants. Non-complexing Gran titrations have the advantage of not adding any complexant, thus reducing waste disposal, corrosion and post-measurement recovery problems. They also reduce the consumption of alkali and hence thus are economical.

3.7. Standard addition of acid in the presence of complexant

Baumann [33,34] developed an ingenious method of adding known aliquots of standard acid to the sample in the presence of potassium thiocyanate (KCNS), measuring the potential and deriving the free acidity by solving three simultaneous Nernst equations. The method was demonstrated for solutions containing Al (III), Cr(III), Fe(III). Hg(II), Ni(II), Th(IV) and U(VI) with [Metal]/[H^+] ratios <2.5 and was suitable for the determination of ∼10 μmol of acid in 10 mL total volume. The accuracies could be judged from the agreement of Nernst slopes in the presence and absence of hydrolysable ions and relative standard deviations were better than 2.5%. KCNS was employed as it is a moderately strong complexant for many hydrolysable metal ions and does not exhibit any buffering action being a salt of strong acid and strong base. The toxicity of CNS^- and the waste disposal problems are the disadvantages of this method.

3.8. Thermometric or enthalpimetric titration

Thermometric or enthalpimetric detection of the end points provide an alternate method for the alkalimetric titrations. The method is especially suited for weak base – strong acid titrations or titrations which use fluoride ions as the complexants which are known to degrade the performance of glass electrodes. Automatic titrators with thermometric end point detection are available commercially and are also easily assembled in laboratory. Bodewig [50] developed an enthalpimetric titration method for the determination of free acidity in simulated nuclear fuel solutions containing Th(IV), U (VI) and Al(III) after precipitating or complexing with excess of KF. The effect of the presence of potassium, barium, strontium, cerium, zirconium and molybdenum was also studied. The method as per the author reports a precision of ±0.01 mol L^{-1} and an accuracy of better than ±0.02 mol L^{-1}. Nevertheless the volume of the waste generated in this method is very large (∼65 mL) and the titration is done with 1 M NaOH. Thus though this method claims possibility of automation and quick measurement, it is not suitable for routine measurements.

Williams et al. [51] applied the thermometric titration to the determination of free acid in plutonium nitrate solutions using potassium fluoride to suppress the hydrolytic interference of plutonium(IV) and could determine 0.2–2.0 meq of free acid with acceptable bias and precision in solutions containing up to 30 mg of plutonium. In contrast, neither the thermometric nor the potentiometric technique was suitable for samples containing more than eight milligrams of plutonium complexed with potassium oxalate.

Miller and Thomason [52] reported a thermometric titration procedure, without any complexant, using NaOH as titrant for the determination of free acid of solutions containing Zr^{4+} in HF, UO_2^{2+} in H_2SO_4 and HNO_3 as well as Th^{4+} in HNO_3, where the heats of hydrolysis of the cations are distinctly different from the heat of neutralization of the free acid. They reported a relative standard error of 1–2% at 95% confidence level for the estimation of 0.1 meq of free acid and Ca. 5% error for the determination of 0.01 meq. This method could not be used for free acid determination in solutions containing Fe(II), Fe(III), Al(III) and U(IV).

Zamek [53] used $Na_2B_4O_7$ or $Li_2B_4O_7$ in a successive thermometric titration of free HNO_3 and UO_2^{2+} (after the addition of aq. H_2O_2) of in tributyl phosphate extracts diluted with dodecane and CCl_4. For 0.100–1.0 M HCl and 0.01–0.2 M UO_2^{2+} the errors ranged from −0.6% to +0.78% and from −1.5% to +2.8%, respectively.

Thermometric determination of the free acidity of solutions containing plutonium, uranium, iron, or a mixture of these elements was reported by Guillot [54].

3.9. Alkalimetric titration using potentiometry

Perhaps the largest number of papers that have appeared on free acidity determination deal with alkalimetric titration using potentiometric follow up of the pH either manually using a pH meter or instruments such as autotitrators, after compelxing the hydrolysable ions with a suitable complexing agent.

Motojima et al. [55] developed a procedure for the sequential determination of the free acidity and uranium using ammonium sulfate as the complexant. The free acid was first determined by potentiometric titration with NaOH to get the first inflection point, the uranyl sulfate complex was broken using hydrogen peroxide to release equivalent amount of acid which was again titrated to get the uranium amount. The method was suitable for samples containing 25 mg to 2 g uranium(VI) and 0.05–30 meq free acid in nitric, hydrochloric or sulfuric acid media and also for the estimation of uranium in TBP/kerosene. Iron and chromium were found to interfere in free acid determination, while zirconium interfered during the uranium determination step due to hydrolysis.

Ahmed et al. [56] modified Motojima's procedure using sodium sulfate instead of ammonium sulfate and sodium carbonate in the place of sodium hydroxide. The method could determine the free acidity and uranium sequentially using an automatic titrator in solutions containing U(VI) and Pu(IV). The method had the advantage of having the end point at a lower pH of <5 which obviously lowered chances of hydrolysis and reported an overall recovery of $>99.5\%$ with a RSD of 0.7% for the free acid and recovery of $>98.5\%$ and RSD of 1.2% for the uranium determination. However the ratio of [U]/[H+] employed by Ahmed et al., was ranging between 0.2 and 8. The free acidity determination in Pu(IV) containing solutions was carried out using a standard addition procedure.

Buijs et al. [57] reported a method for the determination of free acidity by titration with NaOH after complexing with 1.5 M NH_4F. They could also demonstrate semiquantitative determination of plutonium by titrating with NaOH in the absence of NH_4F and from the difference in the titer values in the absence and presence of the complexant.

Potentiometric titration of ~0. 5 mM free acid, 10–50 mg of U(IV), 10–50 mg of U(VI), and ~1 mM hydrazine mononitrate in uranous nitrate solns in PUREX process streams was reported by Emura et al. [58] using alkalimetric titration. The method consists of two procedures. A sample solution (about 80 mg as U) was diluted with g 30–40 mL water and was oxidized by aeration at 50–60° C for 10 min. The U(VI) was masked with 10 mL $(NH_4)_2SO_4$ soln. (232 g/L), and free acid after oxidation was titrated with a 0.2 N NaOH at the rate of 1 mL/min. After the equivalence point for the free acid was obtained, 0.5 mL of HCHO solution was added, and the hydrazine was titrated with 0.2 N NaOH. Another sample solution (about 80 mg as U) was diluted with 10–20 mL H_2O, 10 mL $(NH_4)_2SO_4$ and 10 mL NaF (35 g/L) as a precipitation reagent for U(IV). After the equivalence point for the free acid was obtained, H_2O_2 solution was added, and the liberated acid was titrated with 0.2 N NaOH. The amount of U(IV) was calculated from the difference of the free acid after oxidation and the free acid. The relative standard deviations obtained from six replicate analyses were 1.3%, 1.2%, 0.8%, 1.3%, and 0.6%, respectively, at the concentration levels of 0.61 N free acid, 73.0 mg U(IV)/mL, 74.7 mg U(VI)/mL of U(VI), 0.112 M hydrazine.

Ganesh et al. [59] reported the sequential determination of U(IV), free acidity and hydrazine from a single aliquot. The method involved the determination of U(IV) using fiber-optic UV–vis spectrophotometry, determination of the free acidity by complexing U(IV) with EDTA and titrating with sodium carbonate to pH 3.0, adding formaldehyde to liberate the acid equivalent to hydrazine and continuing titration with same sodium carbonate. They reported an overall recovery of $>98\%$ and a RSD of $\pm 3\%$ for U(IV), nitric acid and hydrazine.

The same authors [60,61] also reported similar procedures for the determination of free acidity and hydrazine sequentially using EDTA complexant and sodium carbonate titrant.

Anwar et al. [62] studied the determination of the free acidity of U(VI) containing solutions using different complexant-titrant combinations viz., NaOH–Na_2SO_4, NaOH–$(NH_4)_2SO_4$ and Na_2CO_3–Na_2SO_4, with $[U(VI)]/[H^+]$ ratios different from those used by Ahmed et al. [56] and concluded that all the combinations result in similar results.

In a continuing study Anwar et al. [63] explored the free acidity determination in the range of 0.05–3.0 meq acid and 20–250 mg U (VI), respectively, by potentiometric titration, using Na_2SO_4 and $(NH_4)_2SO_4$ as complexants and NaOH and Na_2CO_3 as titrants and reported the results as percentage recovery of free acidity and uranium over the range studied. They observed that percentage recovery of free acidity showed a bias varying from –5% to +74% at different free acidity and uranium concentrations for the NaOH–Na_2SO_4, NaOH– $(NH_4)_2SO_4$ and Na_2CO_3–Na_2SO_4 complexant–titrant combinations. The percentage recovery of uranium always showed a positive bias of up to +8% for extreme free acidity-uranium ratios in the case of Na_2CO_3–Na_2SO_4, while the NaOH–Na_2SO_4, NaOH– $(NH_4)_2SO_4$ combinations reported a positive bias of up to only +4%.

Ryan et al. [64] made a systematic study of free acidity determination comparing three methods, viz., which use iodate, oxalate–fluoride and ammonium oxalate as complexants employing alkalimetric titration with an autotitrator especially in high concentration of hydrolysable ions uranyl nitrate and plutonium nitrate. The citrate method was also tested with the samples provided by them in an independent laboratory but was found to give unreliable results. Acid free $Pu(NO_3)_4 \bullet 5H_2O$ was prepared by vacuum evaporation of plutonium nitrate in nitric acid and characterized by studying the weight loss on thermal evaporation. Known weight of this compound was dissolved in standard nitric acid on weight basis to prepare free acid standard. Similarly J.T. Baker reagent grade $UO_2(NO_3)_2 \bullet 6H_2O$ was used to prepare free acid standard by dissolving in standard nitric acid and making up to known volume. Twenty four standard solutions were prepared with free acidity varying from ~0.9 M to ~5.5 M containing mixture of U(VI) and Pu(IV), only plutonium (having 100, 200, 300 and 400 gPu/L) and only uranium (300gU/L). These standards were analyzed using three methods. The first method used iodate as the complexant reported in the literature [7,8] in which the free acidity was determined by adding the sample aliquot to 10 mL of 0.3 M KIO_3, preadjusted to pH 4.3 and titrating back to the same pH. The second method used mixed oxalate–

fluoride (0.75 M $Na_2C_2O_4$–0.26 M NaF) as the complexant preadjusted to pH of 6.99–7.01 and titrated with 0.1 M NaOH to initial pH. The third method was an improved oxalate procedure using 20 mL of 0.15–0.2 M $(NH_4)_2C_2O_4$ (0.1 M was tested and found to be unsatisfactory) as the complexant and titrating with 0.1 M NaOH to the inflection point around pH 6.5 using an autotitrator (Brinkmann Instruments Model E636). The modified ammonium oxalate method was found to give bias values of -0.007 M and -0.008 M with standard deviation values of 0.014 M and 0.021 M for 32 and 20 titrations, respectively for 0.15 and 0.2 M ammonium oxalate concentrations and hence were considered precise and accurate for free acidity determinations.

Ryan et al. [65] reported a method for the determination of free acid in solutions containing uranyl and other hydrolysable ions, based on the complexing of uranium as the oxalate with the oxalate solution cooled to 0 °C prior to potentiometric titration to a predetermined pH. The end point was found to be independent of uranium concentration and occurs at pH 7.0. The Gran mathematical treatment of the pH/vol relation of the titrant curve is shown to be applicable over a wide range of uranium concentration in the oxalate/uranium/nitric acid system.

Sanderson [66] developed a method for the determination of free acidity in aqueous uranyl nitrate solutions using potassium oxalate which complexes the uranium and major impurities and the salt of benzoic acid which possesses a favorable dissociation constant, in addition to a suitable partition coefficient between water and chloroform. By this means, an equivalent quantity of benzoic acid, liberated by the free nitric acid was transferred into the chloroform layer was titrated with alcoholic potassium hydroxide.

Erben et al. [67] reported a differential potentiographic titration procedure for the simultaneous determination of the free acidity and U(VI) concentration in aqueous or organic (trilauryl amine, tri-*n*-butyl phosphate) by mixing the sample with acetone and titrating with NaOH. The amounts of acid and uranium were calculated by means of calibration curves relating these amounts to the position of the peaks on the titration curves.

Tsuji and Yokoyama [68] reported an improvised method for rapid alkalimetric titration of free acidity in U(VI) solutions. In a direct titration of HNO_3 containing U(VI) alone the first equivalence point on the differential titration curve corresponded to free HNO_3. In the titration of the same solution after precipitation of U (VI) by H_2O_2, the equivalence point corresponded to the sum of the free and the U(VI)-bound HNO_3. U(VI) could then be determined from the difference of the two titers. The free acidity in U(VI)–Al mixtures could be carried out with the addition of $(NH_4)_2C_2O_4$. Entire titration could be carried out within 3 min with a relative error of $< \pm 3\%$.

Moeken and Van Neste [69] reported a simultaneous potentiometric indicator method for the determination of free acidity, Fe (III), and U(VI) concentrations in the irradiated fuel reprocessing solutions employing KF as complexant.

3.10. Alkalimetric titration using visual indicators

For routine free acidity estimations in a process control laboratory, alkalimetric titrations utilizing visual indicators have been developed. Uma Sundar et al. [6] used a mixed indicator bromothymol blue and neutral red which indicates end point at pH 7.2 with fluoride as the complexant and methyl red–methylene blue which indicates end point at pH 5.4 using potassium oxalate as complexant to determine the free acidity of uranyl nitrate solutions with a precision of ± 0.02 mol L^{-1}. The results were compared with those obtained with potassium hexacyanoferrate (II) as complexant. They concluded that complexation with oxalate performs better over fluoride in samples containing large amount of silica as fluoride reacts with silica and gives a negative bias. Moreover, the recovery of uranium from analytical waste containing oxalate is easier.

3.11. Non-aqueous titrations

Pillay et al. [70,71] reported a modified method to overcome the interference of the hydrolysable ions by adding alkaline salt (80% m/v) in methanol medium to the sample, which enhances the activity of the protons thus shifting the point of inflection in the titration to a lower pH. Performing the titration in the methanol medium also decreases the hydrolysability of the interfering metal ions. The method was demonstrated to work with especially higher $[M]/[H^+]$ ratios of the order of 20:1, in Fe(III) containing sulfuric acid solutions with good accuracy and precision using magnesium chloride. Attempts to carry out titrations without alkaline salts in cyclohexylamine, pyridine and *t*-butanol media were seen to be severely affected by biased results for the acid recovery with poor inflection points in the titration curve.

Determination of free acidity in plutonium, uranium, and thorium solutions by titrating with NaOEt using phenolphthalein as visual indicator in isopropanol medium after precipitating the actinides as double salts with CsCl was reported by Schmieder and Kuhn [72].

Koch [73] described a potentiometric method for the determination of free acidity and U(VI) in solvents, such as trimethylbenzene containing quaternary ammonium nitrates using hydrogen peroxide to complex U(VI). In tertiary ammonium nitrate solutions extraction into 0. 05 M $NaNO_3$ was carried out prior to titration.

Erben et al. [74] described a simultaneous quantitative determination of free acid and uranium(VI) in aqueous and organic samples by differential potentiographic titration in acetone medium. The amounts of acid and U are calculated by means of calibration curves relating these amts. to the position of the peaks on the titration curves.

3.12. Alkalimetric titration without complexation

Kamat et al. [75] developed a unique direct alkalimetric titration for the determination of free acidity, uranium and nitrate content in a single aliquot. The method is based on the fact that when the first derivative $dpH/d\nu$ is plotted vs the volume of the titrant either NH_4OH or NaOH, three distinct peaks are obtained which by solving three equations provide the concentrations of free acid, total nitrate and total uranium. They reported a RSD of $\pm 0.82\%$ for the determination of uranium and $\pm 1.52\%$ for the determination of nitrate, respectively.

3.13. Electrical conductivity and ultrasonic velocity

Kuno et al. [76] reported the measurement of free acidity using multiple correlation of the electrical conductivity with concentration of uranium, free acidity and the temperature of the solution. The method could be applied to solutions containing uranium from 0 to 100 g/L and acidity range of < 3 M and for the temperature range 20–40 °C. Similarly the ultrasonic velocity was also found to have good correlation with free acidity for uranium concentrations in the range 0–180 g/L, temperature range 15–35 °C and acidity range 1–6 M. Though considered non-destructive and simple these methods are suitable to get only an idea of the concentration levels during the processes and should not be treated as very accurate.

3.14. Alkalimetric high frequency titrations

Menis [77] applied the technique of high-frequency titrimetry to the determination of thorium, uranium, sulfate, and free acid in four parts. In Part I, the reproducibility of the method for the titration of standard solutions that contained 50 mg of thorium in the absence of interferences is established. Under these conditions, the coefficient of variation of the method was $< \pm 1\%$. In Part II, the effect of uranium on the high frequency titration of thorium, as well as the application of the method to actual samples, is discussed. Uranium in a ratio of 5–1 to thorium can be tolerated. When the method is applied to the analysis of representative samples, the coefficient of variation is 1%. Attempts to determine uranium by high-frequency titration with 8-quinolinol were unsuccessful. Tests on this titration and possible reasons for its failure are discussed in Part III. The application of the high-frequency titration method to the determination of sulfate in solutions of uranyl sulfate is described in Part IV. The coefficient of variation, on titrating 40–70 mg of sulfate with barium chloride after the uranium is masked with citrate or fluoride, is $\pm 2\%$. In Part V, the high-frequency titration of free acid in solutions of uranyl sulfate is discussed. Uranium up to 350 mg, which was the highest level tested, does not interfere. The coefficient of variation of the method is $\sim \pm 2\%$.

3.15. Spectrophotometry

Bhargava et al. [78] developed a spectrophotometric method for the determination of the free acidity in nitric and hydrochloric acid solutions of uranyl ions. The method utilized the feature of linear increase in the absorbance of the peaks with maxima at 404, 416 and 426 nm with increase in free acidity in nitric acid solutions. The method is applicable to solutions with free acidity in the range 0.5–4.0 M and does not employ any complexing agents. Among the interfering metal ions studied, viz., Co(II), Ni(II), Fe(II), Fe(III), Ru(III), Rh(III), Cr(VI) and Ce(IV), the last two mentioned above were seen to introduce an error of ± 0.1 M when present at levels up to 0.1% with respect to U(VI). The colored fission products Ru(III) and Rh(III) up to 0.25% as well as Co(II) and Ni(II) up to 5% with respect to uranium(VI) caused no significant error. Fe(III) above 2.5% caused interference. The method was not found to be suitable for solutions with free acidity below 0.5 M due to low absorbance values of U(VI) and above 4.0 M due to the shifting of the maxima to longer wavelengths significantly due to complexation. The method also requires a prior knowledge of uranium concentration for the estimation of the free acidity.

4. Conclusions

It can be seen that from the above review that the methods which employ complexants and alkalimetric titration either using manual titration with visual indication of end point or pH meters appear to be most versatile and attractive with respect to simplicity in execution, acceptable bias and precision and also for the recovery of the metal ions after the free acidity measurement. It can be noticed that mostly researchers have used inflection point as the end point which may increase the possibility of hydrolysis when neutralization occurs at pH 7 or beyond, especially when tetravalent ions are present. Even in the methods which use titration to preadjusted pH attempts to study the bias as a function of end point pH is rare. It also should be noted that the [complexant]/[metal] ratio is as important as [free H^+]/[metal] ratio and this issue is not studied in detail by many. Titration with sodium carbonate provides the advantage of neutralization at a lower pH with a lower possibility of hydrolysis of the metal ion, nevertheless has not been tried by many possibly because the titration usually demands autotitrators and is very difficult to be followed by visual indication.

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