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New Methods for the Determination of Free Acid in the Presence of Large Amounts of Uranyl Salt

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Two new methods have been developed for the determination of free acid in solutions containing large amounts of uranyl salt. Both methods are based upon the weakening of the acidic properties of the uranyl ion which is brought about by its bonding to sulphate ions. By utilizing this complex formation it is in fact possible to arrive at a titration curve of two distinct steps. According to the first method, the free acid is determined by potentiometric titration to the well determinable point of inflexion between these steps. For low concentrations of acid, however, when a titration is not practical, the free acid is instead determined by direct measurement of pH, according to the second method described.

For all methods of aqueous reprocessing of irradiated uranium fuel, the concentration of free acid in the uranyl salt solutions to be treated is one of the most important process variables. Frequent and reliable determinations of this quantity are therefore wanted. On account of the acid properties of the uranyl ion, UO_2^{2+}, these cannot, however, be performed as simple alkalimetric titrations. Even if the concentration of uranyl salt, C_U, is fairly low, the hydrolysis of UO_2^{2+} will be appreciable before the free acid has been completely titrated [1]. Further, direct measurement of the pH of the process solutions by, *e.g.*, the glass electrode is not attractive as the reading will depend very much on C_U. In solutions of low acidity UO_2^{2+} will affect the pH both by acting as an acid and by influencing the activity coefficient of the hydrogen ions. The latter effect is present even in strongly acid solutions, where in any case direct pH measurements are not very suitable because of the large and variable liquid junction potentials.

With increasing C_U, the conditions for the determination of free acid grow worse at a rate much faster than would be expected from the simple rise in concentration of the hydrolyzable species UO_2^{2+}, on account of the increase in

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the degree of hydrolysis at a given pH which is a consequence of the formation of polynuclear aggregates in the solution [1].

In this connection it should be emphasized that the concentration of "free" acid to be determined is by definition the acidity of the solution when the uranium(VI) is present solely as the unhydrolysed ion UO_2^{2+} (or, of course, as complexes formed by this ion). If only anions of strong acids are present, (*e.g.* nitrate, chloride or perchlorate ions) this concentration of free acid, C_H, will be $= [H^+]$, the concentration of hydrogen ions. If however anions of weaker acids are also present (*e.g.* sulphate ions), C_H will be equal to the sum of $[H^+]$ and the concentrations of species of undissociated acid (*e.g.* HSO_4^-). In this latter case, the pH will, of course, depend very much upon the concentrations of the proton accepting anions. If these vary, the possibility of an accurate measurement of C_H by the pH is obviously less than in a solution containing only anions of very strong acids.

In practice, nitrate solutions are by far the most important and they will therefore be the main consideration of this work.

METHODS FOR MEASURING THE FREE ACID IN URANYL SALT SOLUTIONS

A number of methods have been used, or could be conceived, to avoid the interference of uranyl ions with the determination of free acid. However, by dividing according to the principle applied, they fall into a few classes only which are specified below, together with a discussion of their relative merits.

Measurements of pH in salt media, acid enough to prevent hydrolysis of UO_2^{2+}. As has already been stated, accurate values of C_H cannot be obtained by direct measurements of the pH of the process solutions. The position can be very much improved, however, by measuring in the presence of a high and approximately constant concentration of a neutral salt (*e.g.* sodium perchlorate or sodium nitrate). In such solutions, the liquid junction potentials are mostly suppressed and the activity conditions stay fairly constant even if C_U and C_H vary considerably, Thus the values of pH found will give true values of $[H^+]$, and this quantity equals C_H, as long as the hydrolysis of UO_2^{2+} is negligible. In order to determine the range of acidity where this condition is actually fulfilled, the measurements can be arranged as follows [2]. To a slightly acidified solution of a certain C_U, containing a high concentration of sodium salt, portions of a strongly acid solution of the same C_U and salt content are added. After each addition, the pH (*i.e.* $[H^+]$) of the resulting mixture is measured. If the uranyl salt preparation contains free acid, this value of $[H^+]$ will be higher than that calculated from the amount of strong acid deliberately added. At the beginning of the titration, however, still another rise in $[H^+]$ is likely to occur due to a partial hydrolysis of the uranyl salt. As the acidity of the mixture increases, the hydrolysis will be more and more suppressed, and finally its influence on $[H^+]$ will practically cease. As C_U is kept constant, and hence also the amount of acid coming from the original uranyl salt, the virtual suppression of the hydrolysis will be indicated by the appearance of a constant difference between the found and calculated values of $[H^+]$. The free acid contamination of the original uranyl preparation is easily calculated from this difference.

Once the acidity ensuring a complete suppression of hydrolysis is known as a function of the uranyl salt concentration, then the measurements can also be arranged in the following way. A solution is prepared which contains, as well as a high concentration of neutral salt, enough acid to prevent hydrolysis of uranyl ions even if added in considerable concentration. To this solution, another solution is added which has the same content of neutral salt and deliberately added acid, but also contains a fairly high concentration of uranyl salt. As long as the uranyl concentration of the mixture stays within a certain known limit, the increase of $[H^+]$ measured is due to the content of free acid of the original uranyl salt preparation. The increase should be proportional to C_U which gives a good check on the reliability of the measurements.

This method of determining C_H by measurement in solutions where it is simultaneously proved that no hydrolysis exists is certainly the least objectionable one from a theoretical point of view. On the other hand, the procedure cannot easily be adapted to very small samples, as several portions of uranyl solution have to be added in order to ensure a good result. The measurements also require a fair amount of care and time, as the value of pH has to be accurately determined for each point in the series of titration.

It is therefore preferable to use this as a reference method by which other methods more suited to routine work can be checked. As such it has been employed in the present investigation.

Precipitation of uranium(VI) with subsequent conventional alkalimetric titration of acid. As precipitating agents cyanoferrate(II)[3], iodate [4] and hydrogen peroxide [3] have been used. After precipitation, the solution is centrifuged and samples taken from the supernatant solution.

All precipitation methods depend on the assumption that the precipitate is strictly an uranyl compound, *i.e.* no hydrolysis of the group UO_2^{2+} must take place. Moreover, no occlusion of acid is supposed to occur within the precipitate. These conditions are, of course, serious weaknesses common to all precipitation methods. As to convenience, the centrifugation introduces an extra handling step.

Removal of uranium (VI) by means of ion exchange with subsequent conventional titration of acid. If the sample is passed through a cation exchange column, saturated with hydrogen ions, the uranyl ions will be exchanged for an equivalent amount of hydrogen ions. The pure acid solution thus obtained can then be titrated without complications, and C_H is found as the difference between the amount of acid thus found and the amount arising from the exchange which equals $2C_U$ (*cf.* Ref.[5]).

The method therefore presupposes that the C_U of each sample is accurately known. If this concentration is high relative to C_H, the latter quantity will however not be determined very precisely.

Suppression of the hydrolysis of the uranyl ion by means of complex formation, with subsequent potentiometric titration of the free acid. The formation of a metal complex in solution implies as a rule that one or more water molecules in the hydration shell of the metal ions are replaced by the complex forming ligand. The acid properties of the metal ion, which are due to the dissociation of hydrogen ions from the hydration shell, are therefore likely to decrease on complex formation, *i.e.* the hydrolysis at a given pH will generally be less for the complex than for the simple hydrated ion. If the ligand is an anion, the decrease of ionic charge brought about by its association will further decrease the probability of hydrogen ion dissociation from the remaining water of hydration. In such cases the effect of complex formation upon the hydrolysis should thus be especially marked.

In order to be analytically useful for the determination of free acid in solutions of hydrolyzable ions, the effect brought about by the complex formation must be large enough to give a titration curve with two steps which are distinctly separated. In the case of uranyl salt solutions, this means a rather large displacement of the metal ion step. It is therefore necessary to add a ligand which binds practically all uranium(VI) into complexes which are not easily hydrolyzed. Unfortunately, most ligands forming strong complexes with the uranyl ion are also fairly basic and thus convert the strong acid of the solution into weaker acids, thereby displacing the acid steps towards a higher pH region as well. The crucial point is thus to find a ligand combining a strong affinity for UO_2^{2+} with as low a basicity as possible. Once a ligand has been found that really separates the acid step from the uranyl one, then the acid can be determined by a straightforward potentiometric titration. The simple procedure thus arrived at, demanding neither a separation of the uranium nor an exact knowledge of its concentration, makes the complex formation approach the most attractive one for removing the uranium interference. It therefore seems natural to choose this line for further development.

Up till now, oxalate [6-8] and fluoride [9] have been the most widely used complexing agents. The basicity of the oxalate ion is however unsuitably high so that the separation between the acid and uranyl steps is still rather poor. The inflexion point is therefore rather difficult to determine, and if the molar ratio C_U/C_H is high, the value of C_H tends to come out too high. This is especially the case at high uranium concentrations, as has also been shown in the present investigation. Thus if $C_U = 0.84$ M (= 200 g U/l), a significant deviation occurs if the molar ratio exceeds 3 (*cf.* tab. 1). Evidently, oxalate prevents interference from the uranyl hydrolysis only if the conditions are not very severe *. As to fluoride, the attack on glass by acid fluoride solutions will always make it impossible to perform reliable potentiometric titrations involving a glass electrode. One might resort to conductometric titration, though this method seems to work only for rather low concentrations of uranyl salt [9].

Among complexing agents which have so far not been used for the present purpose, the sulphate ion especially seems to be quite promising. Its basicity is fairly low, yet it forms rather strong complexes with the uranyl ion [10], without any tendency to precipitation at high ligand concentrations. In the last respect, the sulphate ion differs favourably from, *e.g.*, oxalate.

In the present investigation, a potentiometric titration method based upon sulphate complex formation has been worked out for the determination of free acid in the presence of even very large amounts of uranyl salt. In order to achieve as good a suppression of the hydrolysis as possible, a saturated ($\approx$ 4

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* Oxalate works better at 0°C than at room temperature [8], but the cooling certainly means a complication in routine work.

M) solution of ammonium sulphate has been chosen as ionic medium, this salt being the most soluble of the readily available sulphates. In this medium, the free acid of samples containing as much as 400 g U/l can still be fairly correctly determined even at a molar concentration ratio uranyl/acid of 5 to 6, as will be described below in greater detail. This implies that acidities as low as 0.3 M can be determined in an almost saturated uranyl solution. For acidities below 0.3 M, the determined value is too low in solutions containing $C_U = 400$ g U/l, but correct at lower C_U. However the quantity of base required for the titration soon becomes inconveniently small for samples of the desired volume.

For samples of low acidity, a new approach, utilizing direct pH measurement in a complex forming medium, is therefore applied.

Measurement of pH in a salt medium where the hydrolysis has been extensively suppressed by means of complex formation. If the salt medium, which is in any case necessary for a successful direct measurement of pH, is chosen so that its anions form strong complexes with the uranyl ion, then it might be expected that the influence of the uranium on pH will be much less than in a non-complexing medium. Therefore, it should be possible to treat a value of pH determined in such a solution as a measure of the free acid content of the sample, even if the uranium/acid ratio is much too high for a successful direct measurement of pH in a medium where no complexes are formed. In the present investigation it has in fact been shown that fairly good values of C_H can be obtained in this way, even for solutions of rather unfavourable composition. As in the titration method just described, the sulphate ion was used as the complex forming ligand, and moreover the same medium, $\approx$ 4 M ammonium sulphate, was chosen. From the measured values of pH correct values of C_H (down to $C_H = 25$ mM) can be calculated directly if $C_U \lesseqgtr 100$ g U/l. For more concentrated uranyl solutions the method can still be used if empirical corrections are applied to the measured values of pH. At least up to $C_U = 200$ g U/l, the corrections are quite modest and presuppose only a very rough knowledge of C_U.

As a measured value of pH corresponds to one single value of C_H once the correction for the influence of uranium (if any) has been introduced, only one measurement is necessary in order to determine the acidity (once the glass electrode has been duly calibrated, as described below). No elaborate titrations with accurate determinations of several pH values are needed, contrary to what is the case if C_H is to be reliably determined by pH measurement in a non-complexing medium, according to the first method mentioned above. As only small samples are wanted ($\leqq 0.2$ ml) and a minimum of manipulation, the present method is especially well suited for highly active solutions. On the whole it is the most suitable method for all samples that contain so little acid that the otherwise more precise titration in sulphate medium is not feasible.

In the following, a detailed description will be given of the two new methods which have been developed in the present investigation. Each of them has so far been used successfully for more than 200 routine analyses.

THE TESTING OF REAGENTS FOR ACID IMPURITIES

Ideally, the salts used in the present investigation should have been free from acidic or basic impurities, but as this could not be guaranteed it was necessary to examine them and determine the exact concentration of any such impurities so that a correction could be made.

The *uranyl nitrate* (Hoboken "nucléairment pure") was tested by pH measurements in an approximately constant ionic medium, according to the first method given above. The second variant of the method was applied, *i.e.* the concentration of uranyl salt in the solution was increased at approximately constant concentration of acid. Titrations were performed at four acidities, ranging from 10 mM to 110 mM. The ionic strength of the medium was 2 M, sodium nitrate being used as the supplementary neutral salt. The temperature was kept constant at 25°C. As was also the case for all other measurements reported in this paper, the values of pH were determined by a glass electrode, in connection with the Radiometer pH Meter pHM 4. As reference, a saturated calomel electrode was used.

In fact, no free acid could be found in the uranyl nitrate preparation within the experimental error of the method applied. This means that the acid contamination, if any, is certainly < 2 % of the concentration of the uranyl ions.

Ammonium sulphate. The value of the pH of a saturated ammonium sulphate solution of the correct stoicheiometric composition was found by potentiometric titration of a slightly acidified solution. Before titration the solution was freed from carbon dioxide by a stream of nitrogen gas.

The inflexion point, corresponding to equivalent amounts of NH_4^+ and SO_4^{2-}, was found at pH $= 5.2 \pm 0.1$. In fact, solutions having $5.0 < \text{pH} < 5.4$ gave the same result when tried in actual titrations. If a preparation has a value of pH outside these limits, it must be adjusted by a small addition of strong base or acid. In order to arrive at a reasonably stoicheimetric composition it was necessary to dissolve the salt without heating the solution. From a solution that had been boiled, so much ammonia had been expelled that the pH afterwards was only 3.20.

No difficulties were met in the measurement of pH in this concentrated salt solution by the glass electrode in the experiments just described, nor in the later ones where uranyl salt was also present.

THE DETERMINATION OF FREE ACID IN AN URANYL SALT SOLUTION BY POTENTIOMETRIC TITRATION IN A SULPHATE MEDIUM

Trying out the most favourable complex forming medium. Preliminary experiments showed that weakly complexing agents, such as nitrate and chloride ions [11], could not create a sufficiently wide interval between the steps of strong acid and uranyl ion in the titration curve, in spite of the fact that such ions do not move the acid step at all toward higher pH. This is evident from Table 1 which gives the results of titrations of 0.2 ml samples of the composition stated, added to 15 ml of the salt media tried. Even in very concentrated salt solutions the found values of C_H are always too low.

As has already been mentioned, decidedly better results were obtained with the more strongly complex forming sulphate ion, in spite of the fact that this agent also moves the acid step towards higher pH. When a 2 M sodium sulphate medium was used, the error was considerably less than for 2 M nitrate, and still better was saturated ammonium sulphate.

Titrations in saturated ($\approx$ 4 M) ammonium sulphate medium. For this medium, an elaborate testing was carried out, using values of $C_U = 400$ and 200 g U/l. In each series, C_H was varied within wide limits. All titrations were performed as before with solutions prepared by adding 0.2 ml of the acid uranyl solution to 15 ml of the neutral salt medium. The concentration of the sodium hydroxide titrant was chosen so that 1 to 3 ml was used.

Table 1. Titrations of free acid in uranyl nitrate solution in nitrate, chloride and oxalate media.

C_U g U/l $\longrightarrow$	400		200	
C_H M $\longrightarrow$	1	0.3	1	0.3
Medium	% error			
2 M $NaNO_3$	−15	−30	...	...
4 M $NaNO_3$	− 7	...	−5	...
6 M $NaNO_3$	− 7	...	−4	...
4 M NaCl	−13	...	...	...
0.43 M $K_2C_2O_4$	+ 10	+ 16	−1	+ 5

Table 2. Determination of free acid in uranyl nitrate solutions by titration in saturated (= 4 M) ammonium sulphate solution.

C_U $\longrightarrow$ g U/l	400			200		
C_H M	C_{Hd} M	δ %	δ_r %	C_{Hd} M	δ %	δ_r %
7.20				7.03	−2.4	2
4.80	4.60	−4.2	2			
	4.65	−3.1				
3.03	2.98	−1.7	2	3.02	−0.3	2
	2.93	−3.3				
2.02	2.04	+ 1.0	3			
	2.02	0.0				
1.00	0.98	−2.0	3	1.02	+ 2.0	3
	0.985	−1.5		0.995	−0.5	
0.500	0.485	−3.0	4			
	0.48	−4.0				
0.303	0.312	+ 3.0	5	0.308	+ 1.7	3
	0.302	−0.3				
	0.295	−2.7				
0.252	0.245	−2.8	5			
	0.245	−2.8				
	0.235	−6.8				
	0.246	−2.4				
0.202	0.195	−3.5	6	0.198	−2.0	4
	0.187	−7.4				
	0.187	−7.4				
	0.185	−8.4				
	0.185	−8.4				
	0.183	−8.9				
0.157	0.125	−17	7			
	0.153	+ 1				
	0.130	−14				

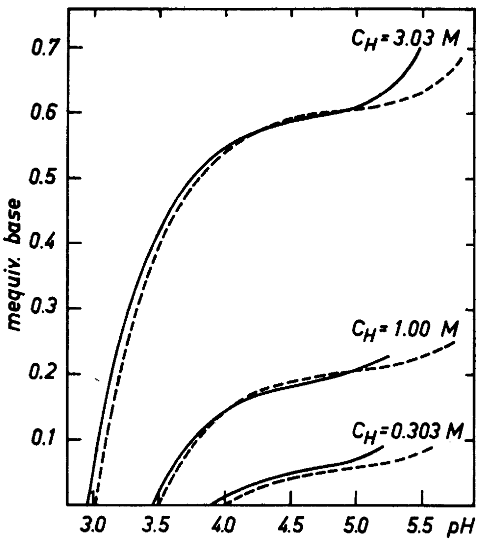

Fig. 1. Titration curves for samples of acid uranyl nitrate solutions in a large excess of saturated ammonium sulphate solution. Samples of 0.2 ml, with the concentrations of nitric acid indicated in the figure, have been added to 15 ml of the ammonium sulphate solution. Fulldrawn and dashed curves refer to samples containing 400 and 200 g U/l, respectively.

In Table 2, the concentrations of acid found, C_{Hd}, are given together with their deviations, δ, from the actual concentrations C_H. The maximum random errors, δ_r, expected to arise under the prevailing experimental conditions are also given. These errors are mainly due to (*i*) the uncertainty in the determination of the inflexion point of the titration curve and (*ii*) the error inherent in measuring the sample aliquot of 0.2 ml. The latter error might be estimated as 1—2 % while the former one varies with C_H and C_U. Its relative amount is roughly inversely proportional to C_H, as the slope of the titration curve is practically independent of C_H, and the absolute error (expressed in equivalents of base) in the determination of the inflexion point is therefore the same for all values of C_H. The error becomes larger with increasing C_U as the uranyl step then comes closer to the strong acid step which results in a steeper slope of the curve between them. In Fig. 1, some titration curves are given in order to illustrate these points.

As is evident from Table 2, the deviations found are of the same magnitude as the estimated values of δ_r down to $C_H = 0.3$ M for the series of $C_U = 400$ g U/l, though the negative deviations seem to preponderate somewhat over the positive ones. For values of $C_H = 0.3$ M, the negative deviations become significant. For such extremes of the ratio C_U/C_H, not even the strong complex formation in a concentrated sulphate solution is sufficient to ensure a good determination of C_H.

For $C_U = 200$ gU/l, the present method works well over the whole range of C_H investigated, down to $C_H = 0.2$ M (Table 2).

For comparison, some of the test solutions were also titrated according to the oxalate method mentioned above, which uses a 0.43 M oxalate solution (80 g $K_2C_2O_4 \cdot H_2O$/l) as complex forming medium. The results (Table 1) show that large positive deviations are found for solutions which are correctly determined by the sulphate method.

THE DETERMINATION OF FREE ACID IN AN URANYL SALT SOLUTION BY pH MEASUREMENTS IN A SULPHATE MEDIUM

A prerequisite for every reasonably accurate determination of C_H from pH measurements is careful calibration of the glass electrode. Preferably, the calibrations should be arranged in such a way that the electrode need not afterwards be transferred to another solution for the main measurement. Such a transfer, with accompanying partial drying *etc.*, is apt to cause small alterations in the asymmetry potential of the electrode, which encroach upon the precision of the measurement. In the present work, the following procedure was therefore adopted. To V ml saturated ammonium sulphate solution, v_1 ml of an a M nitric acid was added and the pH value of the resulting solution measured. As soon as a stable value ($= \mathrm{pH}_O$) had been read for this calibration mixture, v_2 ml was added of the acid uranyl solution to be tested and the new value of pH ($= \mathrm{pH}_U$) measured. The difference $\Delta\mathrm{pH} = \mathrm{pH}_O - \mathrm{pH}_U$ is a function of the concentration of free acid of the uranyl solution, C_H, and to some degree also of C_U, if the hydrolysis of the uranyl group is not completely suppressed. If it is, the value of pH found should agree with that value which is calculated in the following way.

If $[\mathrm{H}^+]_O$ and $[\mathrm{H}^+]_U$ are the hydrogen ion concentrations of solutions after the addition of v_1 and v_2 respectively, then

$$\Delta\mathrm{pH} = \log[([\mathrm{H}^+]_U/[\mathrm{H}^+]_O) \tag{1}$$

Table 3. Calculation of free acid in uranyl nitrate solution from values of pH measured in saturated (= 4 M) ammonium sulphate solution.

	$C_U \rightarrow$ g U/l	0		50		100		200	
C_H mM	Δ pH calc.	δ	C_{Hd} mM	δ	C_{Hd} mM	δ	C_{Hd} mM	δ	C_{Hd} mM
		v_1 = 1 ml		a = 20 mM				v_2 = 0.2 ml	
25	0.091	0.000	25.0	−0.019	19.7	−0.004	23.9	0.033	34.9
50	0.170	0.000	50.0	−0.007	47.6	−0.010	46.5	0.019	57.0
100	0.295	−0.003	98.6	−0.008	96.3	0.006	103	0.020	109
150	0.392	−0.003	148	−0.020	139	0.010	156	0.029	167
200	0.471	0.010	207	0.000	200	−0.010	193	0.046	233
250	0.538	−0.011	241	−0.015	238	−0.012	240	...	...
	$C_U \rightarrow$ g U/l	0		200		400			
		v_1 = 0,5 ml		a = 100 mM		v_2 = 0,5 ml			
50	0.162	0.008	52.5	0.040	65	0.084	82		
100	0.287	0.009	104	0.036	117	0.081	141		
150	0.384	0.011	157	0.011	157	0.070	194		
200	0.463	0.015	210	0.044	231	0.048	235		

The corresponding total concentrations of acid ($= [\mathrm{H}^+] + [\mathrm{HSO}_4^-]$) are called C_{HO} and C_{HU}. As $V[\mathrm{SO}_4^{2-}] >> v_2\ C_H$, the concentration of sulphate ions is virtually constant during the measurements which implies that $[\mathrm{H}^+]_U/[\mathrm{H}^+]_O = C_{HU}/C_{HO}$. As $C_{HO} = v_1a/(V + v_1)$ and $C_{HU} = (v_1a + v_2C_H)/(V + v_1 + v_2)$, the following expression for pH results:

$$\Delta\,\mathrm{pH} = \log \frac{(v_1a + v_2C_H)\ (V + v_1)}{v_1a\ (V + v_1 + v_2)} \tag{2}$$

In the present experiments, a value of $V = 15$ ml has been chosen. As to a, v_1 and v_2, two different sets of values have been used, as stated in Table 3. In this table, the results of the tests performed are given in a summarized form. For each solution, only the mean value is stated out of at least two and often up to five measurements actually carried out. The table first contains the values of ΔpH, calculated according to eqn. (2) for each value of C_H used. Then the differences δ between the (mean) values of ΔpH actually measured and those calculated are tabulated for each solution, and finally C_{Hd}, the concentrations of acid found from the *measured* values of ΔpH. Two series have been performed with solutions free from uranium. From the values of δ found in these series, as well as from the reproducibility of pH for the individual solutions, it seems realistic to reckon an error of at least $\pm$ 0.015, or rather $\pm$ 0.020 units in the determination of pH. The error seems to be about the same in the whole range of C_H measured. The corresponding relative error in C_H depends upon the relation between the amounts of acid added for calibration, v_1a, and that added with the sample, v_2C_H. With the volumes and concentrations used here, an error of 5—7 % should be expected at $C_H = 250$ mM, increasing to $\approx$ 20 % for $C_H = 25$ mM.

The values of pH actually found for the series of $C_U = 50$ and 100 g U/l do not deviate more from those calculated than can be explained by the random errors. For unknown samples of $C_U \leqq 100$ g U/l, correct values of C_H can thus be calculated according to eqn. (2), direct from the measured value of pH, as has already been stated above. For $C_U = 200$ g U/l, however, a significant deviation of $+$ 0.03 pH units appears. For $C_U = 400$ g U/l, a rather large deviation is found, evidently decreasing for increasing acidity of the solution, which is also to be expected.

The determination of nitric acid in a solution of uranyl nitrate in tributyl phosphate — kerosene. The direct measurement of the pH can be used also for the determination of acid in the TBP-kerosene solutions of the Purex process. Because of the small volume v_2 of the organic sample added, an almost complete extraction of the acid into the sulphate solution will always take place. Once extracted, the acid can be determined exactly in the same way as described above. The small amount of organic solvent present does not seem to impair the function of the electrodes.

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