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THE ACIDIMETRIC ESTIMATION OF FLUORIDE.
A COMPARISON OF THE GLASS WITH THE LANTHANUM FLUORIDE ELECTRODE

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SUMMARY

A rapid potentiometric titration using cerium (III) chloride as titrant with a glass electrode indicator system is proposed for fluoride estimations. The alkali fluoride (0.002-0.02 M) initially adjusted to a pH of 6.3 ± 0.05 is titrated continuously. The equivalence point is measured directly from the recorder chart as the mean of two well defined points. Calibrations are carried out with fluoride solutions of about the same salt content, or by repeating the titration on another aliquot with a standard addition of fluoride. This procedure gives results as precise as those obtained previously with the fluoride electrode without elaborate computations. A direct comparison of glass and fluoride electrode systems with different titrants is provided.

INTRODUCTION

The use of lanthanum fluoride crystal electrodes as indicators for fluoride ions [1,2] has largely replaced the use of colour indicators in volumetric analyses for fluoride. However, the electrode method is not an absolute one because the obvious end-points, at inflections or projections of titration curves, differ from equivalence points for precipitation of stoichiometric fluorides in a manner which varies with experimental conditions such as salt or buffer concentration, rate of titration etc. quite apart from variability of junction potentials and the change in fluoride electrode response with time. The electrode method ultimately relies on either a strict comparison of electrode response in the unknown solution with that in a simulated standard fluoride solution, or the extra response produced by standard additions. If it is accepted that the fluoride electrode is used semiempirically, then reasons for selecting it in preference to another indicating electrode should be utilitarian rather than theoretical.

In general the conversion of soluble into insolube fluorides is accompanied by changes in acidity. Alkali fluorides, as salts of strong bases with a weak acid, hydrolyse to give basic solutions; conversely the usual titrants, as salts of strong acids with weaker bases, form acidic solutions. Titrations between them resemble acid-base titrations although a number of processes are involved. The pH decreases initially as the fluoride ion is removed and finally as the precipitated fluoride undergoes hydrolysis. Because all fluorides can be converted to alkali fluorides by standard methods of fusion and hydrolysis, a simple pH titration should serve as a universal finish in titrimetric analysis of fluoride. In this paper we show that the ordinary glass electrode is a satisfactory substitute for the costly lanthanum fluoride electrode in volumetric estimation of fluoride with the usual titrants. We have applied the method to estimate the fluoride produced on hydrolysis of sulphuryl and perchloryl fluorides for which we could check the accuracy by independent acidimetric titration of excess alkali used in these hydrolyses [3]

Acidimetric titrations have been reported previously with thorium nitrate [4] and aluminium alum [5] neither of which in our opinion are satisfactory titrants, but no direct comparison has been made with the fluoride electrode method.

EXPERIMENTAL

All solutions were made with singly distilled water in equilibrium with the atmosphere. Sodium fluoride (AR) was recrystallised from aqueous-alcoholic solution and dried at 150°. Approximate $Th(NO_3)_4$, $La(NO_3)_3$ and $CeCl_3$ titrants were made from hydrated salts. The first two were analysed by decomposing them to oxides at 1,000°C, the last by E.D.T.A. titration. A $CaCl_2$ titrant was made by dissolving calcite (AR) in an equivalent quantity of hydrochloric acid.

Titrations were performed at room temperature using a Metrohm automatic titrator (E 336A) fitted with a 20 ml piston burette. A combined glass-Ag/AgCl electrode system with ceramic salt bridges was employed for pH measurements and an "Orion" fluoride ion electrode and calomel electrode connected via a KCl-agar salt bridge for pF measurements.

Weighed aliquots of standard fluoride stock solutions were taken to some of which were added salt solutions before making up to volume. The solution pH was adjusted to pH 6.3 ± 0.05 with dilute acid and then titrated at constant speed of delivery and at a constant rate of mechanical stirring. Delivery speeds were usually adjusted to give titration times of about 10-15 minutes. Titration end-points were measured directly from graphs to the nearest 0.01 ml on an abscissae scale of 2 cm ml^{-1}. They were taken at A) the intersection of the curve with a line midway between two tangent lines at about 45° to the titration curve drawn using a ruled transparent guide, and B) the intersection of the extrapolated maximum and final slopes. (See Figure 1)

Direct comparison between the glass and fluoride electrodes was obtained by having both electrode systems in the same fluoride solution. The voltages generated were fed into separate pH meters (Pye Model 290) the amplified outputs of which were adjusted to produce the same voltage span for each electrode system when applied to a twin pen recorder. The pH and pF curves could then be superimposed by a small lateral displacement as shown in Fig 4.

The effect on the titration of adjusting the initial pH of fluoride and titrant solutions was examined. Effects of salt additions and titration speeds were also studied in separate experiments.

Fluoride distillations were carried out on 25 ml of 0.1M NaF solution, to which 40 ml of H_2SO_4(1:1) were added, by the Willard-Winter procedure. About 220 ml of distillate were collected and diluted to 250 ml. Titrations were made on aliquots containing about 10 mg fluoride before and after distillation.

RESULTS AND DISCUSSION

The results for pH titrations of pure sodium fluoride solutions with four titrants are given in Table 1 together with the results of a pF titration with lanthanum nitrate for comparison. Typical titration curves are shown in Fig 1. It can be seen that the mean end-point (A+B)/2 agrees with the equivalence point for three of the titrants within the standard deviation. The pH titration curves clearly follow Lingane's pF curves [2] with the four titrants. (They are related by a 180° rotation about a vertical axis through the equivalence points). With $CaCl_2$ as titrant a just perceptible inflection could be observed in aqueous fluoride solution. The solubility of CaF_2 had to be reduced by adding ethanol to get distinct inflections. (The $CaCl_2$ titrations in Table 1 were made in 1:1 ethanol-water mixture). The solubility of aluminium fluoride is much greater so that Chilton and Horton [5] had to carry out pH titrations at higher fluoride concentrations (circa 0.05M) using potassium alum as titrant. These titrants are unsatisfactory both because hydrolysis of the fluorides causes a drawn-out change in the titration curve which makes location of point B less precise, and the need to add alcohol. The most acidic titrant $Th(NO_3)$, which had a pH of 2.76, gave the largest change in pH but the end-point A was difficult to position because of the steep increase in acidity from the start of the titration. The equivalence points were closer to end-points B.

Addition of alcohol gave no improvement in end-point reproducibility. Attempts to reduce the initial drop in pH by raising the pH of the titrant ran into difficulty because of precipitation of hydroxo-species. Further drawbacks with this titrant include dependence on the rate of titration due to ageing of the precipitate; and artefacts on the titration curves produced when the precipitate adhered to the electrode surface and then started to re-dissolve

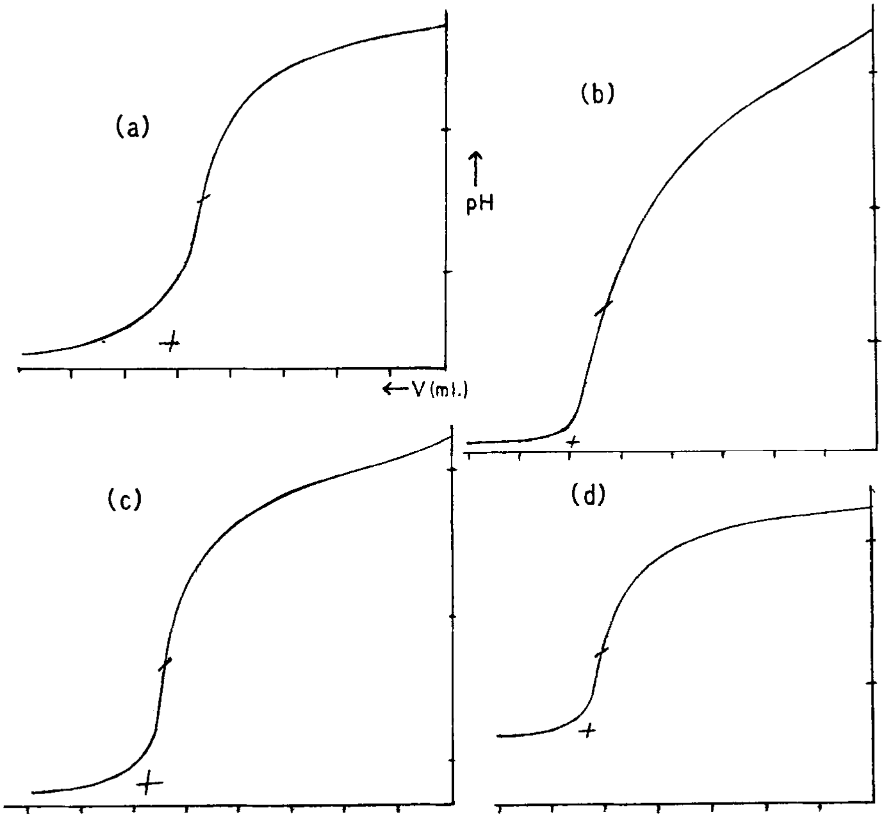

Figure 1 Titration curves obtained with various titrants using glass electrode

(a) $CaCl_2$ (50% ethanolic solution) (b) $Th(NO_3)_4$

(c) $La(NO_3)_3$ (d) $CeCl_3$

when excess thorium was added. The thorium nitrate is also unsatisfactory giving a standard deviation two to three times greater than with other titrants.

Solutions of lanthanum and cerium(III) salts gave well defined end-points which were little affected by titration speed although the overall voltage span was less than with thorium solutions. The mean end-point (A+B)/2 was in good agreement with the equivalence point in the range 0.003 to 0.020 M fluoride. (Titrations at the milli-molar level also gave clear end-points but are excluded because titrant volumes could not be read to the required accuracy). Cerium(III) chloride is preferred to the lanthanum titrant because it seems less prone to give precipitates which foul the electrode surface and give artefacts on titration curves.

TABLE 1

Titrations of sodium fluoride solutions

		Titre to reach end-point for unit weight of NaF soln (ml g^{-1})				
Titrant	NaF soln. (g)	(A)	(B)	(A+B)/2	Mean	Calculated
a) pH titrations						
	3.974 (1)	0.964	1.034	0.999		
$CaCl_2$	5.014	0.963	1.027	0.995	0.992	0.994
(0.05018M)	7.024	0.965	1.012	0.989	(σ = 0.006)	
	10.009	0.964	1.007	0.986		
	3.732 (1)	1.005	1.053	1.029		
	3.729	1.008	1.051	1.030		
$CeCl_3$	4.996	1.009	1.047	1.028	1.032	1.030
(0.03237M)	4.732	1.023	1.057	1.040	(σ = 0.004)	
	4.996	1.017	1.049	1.033		
	9.990	1.020	1.046	1.033		

(continued on facing page)

TABLE 1 (cont.)

		Titre to reach end-point for unit weight of NaF soln (ml g^{-1})				
Titrant	NaF soln. (g)	(A)	(B)	(A+B)/2	Mean	Calculated
	3.013 (2)	1.108	1.168	1.139		
	4.065	1.124	1.161	1.143		
$La(NO_3)_3$	5.014	1.119	1.155	1.137	1.141	1.137
(0.02932M)	7.035	1.130	1.164	1.147	(σ = 0.004)	
	9.952	1.129	1.151	1.140		
	1.994 (1)	1.143	1.299	1.221		
	3.979	1.147	1.249	1.198		
$Th(NO_3)_4$	4.007	1.160	1.250	1.205	1.195	1.231
(0.02026M)	4.952	1.144	1.236	1.190	± 0.014*	
	4.988	1.133	1.239	1.186		
	9.962	1.123	1.211	1.167		
b)pF titrations						
	9.990 (3)	0.3403	0.3723	0.3563		
$La(NO_3)_3$	20.170	0.3456	0.3585	0.3521	0.3515	0.3544
(0.04480M)	38.27	0.3446	0.3542	0.3494	(σ = 0.004)	
	54.05	0.3451	0.3515	0.3483		

(1) 4.191 g NaF/1

(2) 4.201 g NaF/1

(3) 2.000 g NaF/1

* mean deviation

initial volumes were ~ 40 ml in the pH titrations and ~ 80 ml in the pF titrations

(A) and (B) are defined in the experimental section

Calibrations made with pure sodium fluoride solutions cannot be applied when other salts are present if the same accuracy is required. Addition of salts to fluoride solutions reduced the span of pH and pF values and reduced the maximum slope unsymmetrically about the mean end-point. (See Fig 2 and Table 2). Points A and B separate and (A+B)/2 alters from that in pure fluoride solutions. Typically end-points based on calibrations with sodium fluoride solutions can be 1% in error when salt concentrations reach the 0.1M level. For non-complexing anions the effect is mainly a lowering of effective concentration but note that perchlorate is more effective than chloride. The activity coefficient decreases and the fluoride solution becomes equivalent to a more dilute pure fluoride solution. The addition of sodium carbonate was studied because carbon dioxide from the atmosphere is slowly absorbed in the alkali hydroxide solution used in calorimetry [3]. The effect produced is partly due to buffering by the HCO_3^- ion and quite possibly to complexing of the lanthanide ions. The complexing of lanthanium fluoride with carboxylic acid buffers is well documented [6] indeed exposure of the fluoride ion electrode to these buffers can alter drastically the electrode response. Hence solutions above pH 8 are best decarbonated by acidifying to pH 1 and stirring vigorously

TABLE 2

Effect of salts on voltage spans during titration of fluoride with $CeCl_3$ (0.05 M)

Salt added	Conc./M	ΔpH (equiv. mv at 20°C)	ΔmV (F electrode)
-	-	2.40	
		(139.2)	218
NaCl	0.10	2.20	
		(127.6)	192
NaCl	0.01	2.36	
		(136.9)	215
NaCl + Na_2CO_3	0.10 + 0.02	1.80	-
		(104.4)	

before adjusting to the starting pH 6.3. For the most accurate results the calibration should be carried out with a good approximation to the salt content of the unknown solution. Alternatively the titration can be repeated on a further aliquot after a standard addition of fluoride. The addition of swamping amounts of electrolyte is unsuitable because the end-points become more difficult to locate precisely.

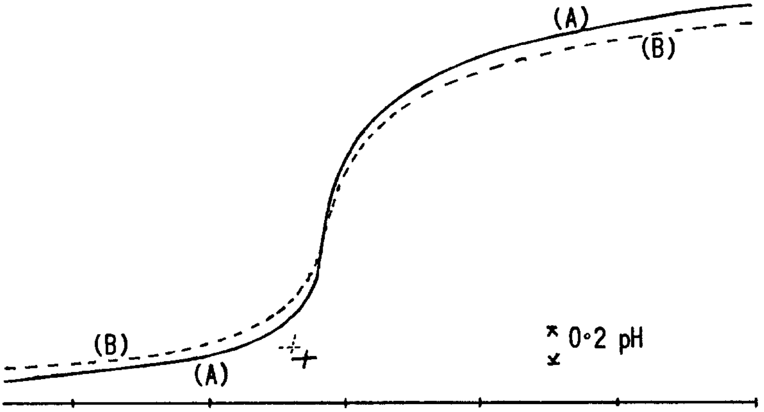

Figure 2 Effect of salt additions on titration curves with glass electrode

(A) Pure NaF (B) NaF + NaCl(0·1 M) + $NaClO_4$(0·01 M)

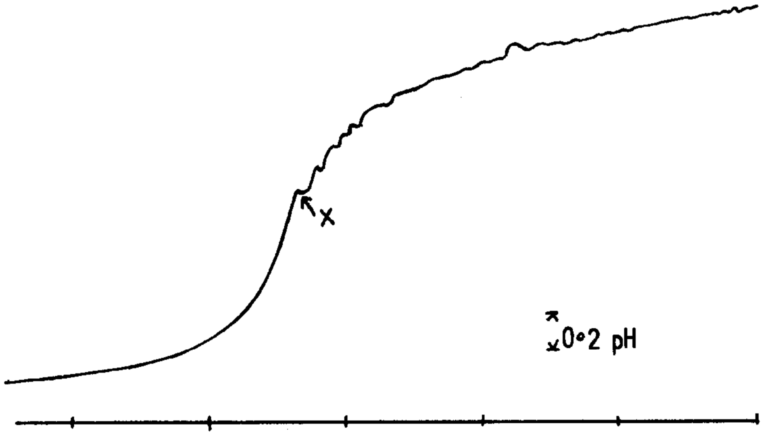

Figure 3 Fast titration of NaF with $CeCl_3$. Titration rate 6·5 ml min^{-1}. Solution clears at point X

Titrations were little affected by quadrupling the usual addition rate of 0.5ml min^{-1}, but excessive rates can produce unstable voltage responses. In Fig 3 cerium(III) chloride was added at 6.5ml min^{-1} and the initial opalescence formed gave way to a clear solution without any precipitation.

TABLE 3

Effect of salt additions on titres with $CeCl_3$ as titrant

NaCl	$NaClO_4$	Titres ml g^{-1} NaF solution		
/M	/M	A	B	(A+B)/2
Glass electrode				
0	0	0.519	0.550	0.535 (σ = 0.004)*
0.02	0	0.522	0.564	0.542
0.04	0	0.528	0.555	0.542
0.10	0	0.523	0.564	0.543
0.20	0	0.526	0.555	0.541
0.02	0.01	0.528	0.572	0.550
0.10	0.02	0.02	0.532	0.554
Fluoride electrode				
0	0	0.320	0.340	0.330
0.05	0	0.318	0.344	0.331
0	0.01	0.323	0.342	0.332
0.05	0.01	0.321	0.345	0.333

NaF 0.1M ; $CeCl_3 \sim$ 0.033M

* Mean of four titrations

A direct comparison of the glass and fluoride electrode response in the same solutions is illustrated in Fig 4. There are distinct differences. The fluoride electrode is more affected than the glass electrode by salt addition, and the glass electrode curves are better shaped for the tangent drawing needed to define end-point A. Different equilibria are involved for each electrode.

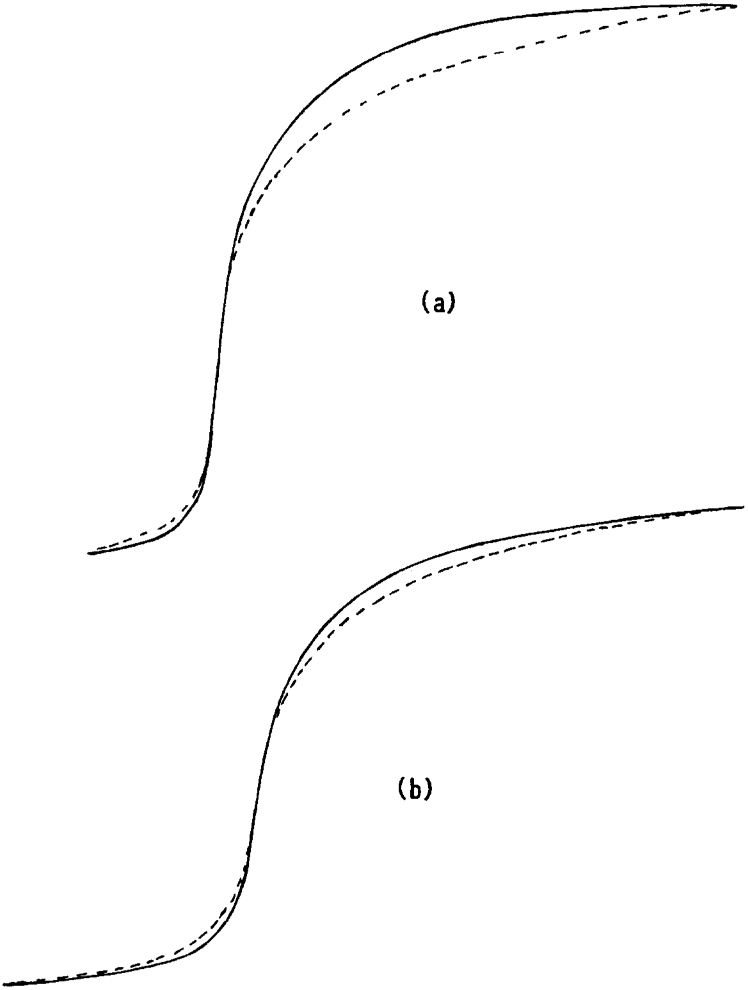

Figure 4 Comparison of glass (full line) and fluoride (broken line) electrodes adjusted to same voltage span

(a) Pure NaF solution adjusted to pH 6•3 ΔpH = 2•4, Δmv=218

(b) NaF + NaCl(0•1 M) +NaClO$_4$(0•01 M) ΔpH=2•2 , Δmv=192

For the fluoride electrode the dominant reaction which is removing fluoride ion before the equivalence point is

$$Ce^{3+} + 3F^{-} \rightleftharpoons CeF_3(s)$$

and a straight line is expected when the Gran function (Vo + V) $[F]^-$ is plotted against volume (V) added to the initial volume (Vo) and $[F]^-$ is calculated from the Nernst equation. After the equivalence point the free cerium ion concentration increases and because this is linked to $[F]^-$ by the above equation the appropriate Gran plot (Vo + V) $[F]^{-3}$ is now supposed to be linear [7]. This is shown in Fig 5 obtained from one of our titration curves. Only the first plot is linear. (A changing slope is evident on a larger scale and a least square plot is required to define the exact extrapolation to a zero value) The second plot is non-linear and on an entirely different scale. The precipitate is not in equilibrium after the short time taken for titration. Equilibration times of up to 70 hours have been shown to be necessary [8].

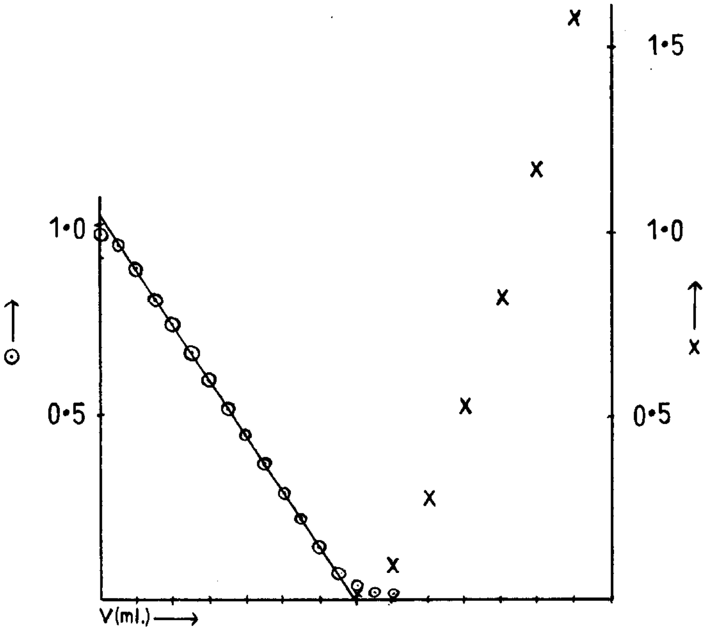

Figure 5 Gran function plots for NaF solution titrated with $CeCl_3$ $F_1 = (V_0 + V)[F^-] = \odot$

$F_2 = (V_0 + V)[F^-]^{-3} = X$

Ratio of scales $F_2 : F_1 = 10^{10}$

The linear regression method, only possible with the fluoride electrode, is no more accurate than the direct measurement of the mean end-point on the graph unless excessively long times are spent on the titrations. Also because only a small part of the emf span is utilized (for $V<0.5$ equiv) the voltage has to be measured more accurately and the temperature more closely controlled if the precision is to be meaningfully compared with the glass electrode results.

For the glass electrode the initial pH is controlled by the fluoride ion hydrolysis and ionization of hydrogen fluoride.

$$F^- + H_2O \rightleftharpoons HF + OH^- \qquad K_h = K_w/K_a$$

$$HF \rightleftharpoons H^+ + F^- \qquad K_a$$

In unadjusted sodium fluoride solutions the pH is given approximately by

$$pH = 0.50\ (pK_w + pk_a + \log c)$$

when c is the fluoride ion concentration and the initial part of the curve would vary logarithmically as c decreased. (Fig 6a) In practice CO_2 absorption from the atmosphere would modify this curve and hence it is advisable to reduce the initial pH. The effect of adjusting the initial pH of an 0.02M NaF solution to pH 6.3 from the calculated pH 7.65 is to produce an almost linear initial curve (Fig 6b) up to $V \sim 0.6$ V equiv. This is due to the acid dissociation of hydrofluoric acid when fluoride ion is precipitated as CeF_3. The flattening of the curve caused by adjusting the titrant to pH 6.3 (Fig. 6 c) is due to hydrogen ion removal via

$$Ce(OH)^{2+} + H^+ \rightarrow Ce^{3+} + H_2O$$

where the hydroxo-ion arises from the $CeCl_3$ hydrolysis. The effect of raising the titrant pH even higher is shown in Fig 6d but these solutions are unstable and in time precipitate cerium hydroxide or hydroxo-chloride species.

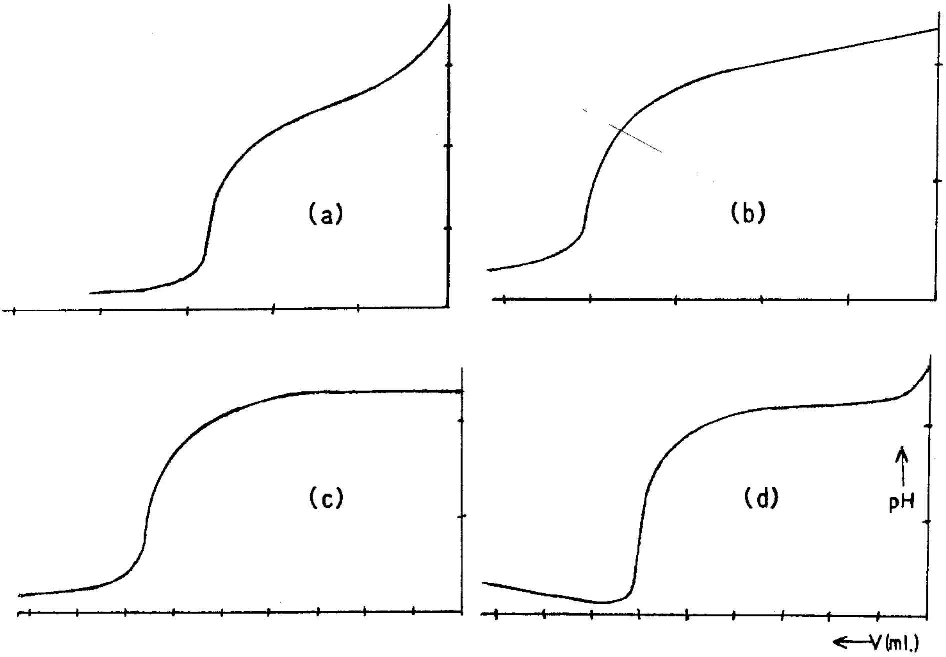

Figure 6 Effect of initial pH of NaF and $CeCl_3$ solutions on the shape of the titration curves

(a) NaF pH=7•5 $CeCl_3$ pH=4•0 (b) NaF pH=6•3 , $CeCl_3$ pH=4•0

(c) NaF pH=6•3 = pH $CeCl_3$ (d) NaF pH=7•6 , $CeCl_3$ pH=7•5

The important practical point is that in all the titrations shown in Fig 6 the overall pH change around the equivalence point varies little with initial and final pH and hence a choice of conditions is available. An initial pH of 6.3 gives a well shaped titration curve without danger of carbon dioxide absorption. Some results of varying the pH of fluoride or titrant are collected in Table 4.

TABLE 4

Effect on end-points of varying the pH of sodium fluoride and cerium (III) chloride titrant solutions

0.1M NaF solution		Titrant	Titre (mlg^{-1} NaF soln.)			Point B
(g)	initial pH	pH	A	B	(A+B)/2	pH
20.03	6.30	4.00	0.640	0.663	0.651	4.20
22.23	7.80	4.00	0.642	0.663	0.653	4.24
12.24	6.30	4.00	0.636	0.672	0.654	4.26
12.41	7.60	4.00	0.641	0.675	0.658	4.28
20.70	6.32	6.30	0.641	0.666	0.653	4.26
*15.10	7.50	7.53	0.807	0.834	0.820	5.08

* Hydroxo-species precipitating from solution.

Superimposed on the initial dissociation of hydrogen fluoride is the production of hydrogen ions by hydrolysis of cerium. Anfalt and co-workers [7] assume that only the metal ion is hydrolysed but the simple experiment of placing cerium(III) fluoride in distilled water shows that the precipitate itself is subject to hydrolysis. In fact the final pH of the solution obtained in titrations (see Table 4) approaches that of cerium(III) fluoride in distilled water (pH 4.2). Because OH^- is isoelectronic with F^- it is quite easy to replace F^- by OH^- and indeed the fluoride electrode is responsive to OH^-. Hence mixed species would be expected which would be subject to mass action by fluoride or hydrogen ion concentrations. The following equilibrium which exclude polynuclear species such as $Ce_3(OH)_4^{4+}$ are amongst those involved

eg $CeF_3 + H_2O \rightleftharpoons CeF_2(OH) + HF$

$CeF_2(OH) + H_2O \rightleftharpoons CeF(OH)_2 + HF$

$HF \rightleftharpoons H^+ + F^-$

Near equivalence the high H_2O/F^- ratio favours the hydrolysis whereas excess F^- suppresses it. After equivalence the excess of cerium could complex the fluoride liberated by hydrolysis as CeF_2^+ and CeF^{2+}, which would further increase the hydrolysis. In the absence of stability constants for mixed species it is not possible to calculate the pH variation during the titrations and Gran plots which are a function of $[H]^n$ where n is integral are not linear. It is interesting to note that Anfalts' excellent fitting of titration curves with stability constants cannot confirm the particular species postulated in solution [7]. Eriksson and Johansson showed subsequently that the thorium nitrate titrant had not reached equilibrium with fluoride before or after the equivalence point [8]. With lanthanum, and presumably cerium salts, equilibration is rapid up to the vicinity of the equivalence point but not after. Hence the fit obtained with "equilibrium" constants is accommodated in the values given to these constants. Other workers have already postulated mixed complexes. Thus Aksel'rud and Spwakovskii give evidence for a hydroxo-chloride as cerium(III) chloride is made alkaline [9] and Sarma and Davis suggest hydrolysis of CeF_2^+ and CeF_3 to $CeF(OH)^+$ and $CeF_2(OH)$ respectively [10]. (The latter work is dubious because equilibration was assumed to take place in 2 minutes).

Finally before the glass electrode titrations can be of general use it was necessary to confirm that they work with distillates from the Willard-Winter method. The exact composition of these distillates is still unsettled and seems likely to vary with the displacing acid and the kinetics of fluoride attack on glass surfaces [11,12]. The shapes of conductimetric titration curves obtained before and after distillation, with lanthanum acetate as titrant, were quite different [13]. However there was no difference in the form of the pH titration curves before and after distillation obtained by our standard procedure. Presumably any fluorosilicate is decomposed in the initial titration and is titrated in the same way as free fluoride. (See Table 5). Co-distillation of strong acid does not affect the titration provided it is neutralised.

TABLE 5

Titrations with $CeCl_3$ (~ 0.03 M) before and after Willard-Winter distillation of fluoride.

	Titre/g of NaF solution (ml g^{-1})				Mean
Original solution	1.046,	1.051			1.049 ± 0.003
Distilled solutions	1.046,	1.052,	1.054,	1.044,	1.049 ± 0.004

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