

# Determination of Fluoride in the Presence of Tetravalent Metal Ions With an Ion-selective Electrode: Application to Raw Materials of Fluoride Glasses

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The performance of masking reagents, viz., ethylenediamine-*N,N,N',N'*-tetraacetic acid, *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid, diethylenetriamine-*N,N,N',N',N''*-pentaacetic acid (DTPA) and triethylenetetramine-*N,N,N',N'',N''',N'''*-hexaacetic acid (TTHA), was studied for the determination of fluoride in the presence of Hf<sup>IV</sup> and Th<sup>IV</sup> using an ion-selective electrode. Hafnium(IV) was effectively masked using an excess of DTPA at pH 6. TTHA was the best reagent for masking Th<sup>IV</sup>, while DTPA provided an alternative for fluoride concentrations of  $<1 \times 10^{-5}$  mol dm<sup>-3</sup>. The masking reaction was rapid and contamination from membrane-dissolution was negligible. Fluoride contents in raw materials of fluoride glasses, viz., ZrF<sub>4</sub>, HfF<sub>4</sub>, and ThF<sub>4</sub>, were determined.

**Keywords:** Fluoride determination; ion-selective electrode; fluoride glass; hafnium masking; thorium masking

## Introduction

Since the discovery of heavy metal fluoride glasses (HMFGs) by Poulain *et al.*,<sup>1</sup> extensive research and development programmes have been carried out to investigate their application to infrared optics.<sup>2</sup> The optical performance is adversely affected by contaminants having an OH group, owing to strong absorption at 2–3  $\mu$ m. Among the raw materials of HMFGs, glass formers, such as ZrF<sub>4</sub>, HfF<sub>4</sub> and ThF<sub>4</sub>, are highly hygroscopic and must be prepared and handled so that they contain a minimum amount of water. Although the determination of oxygen is straightforward in order to assess the quality of these raw materials, special techniques are required, such as charged particle activation analysis.<sup>3</sup> The determination of fluoride as a major component is complementary to the results.

For fluoride determination, potentiometry with an ion-selective electrode (ISE) in conjunction with masking reagents for metal ions is simple and has been widely used.<sup>4</sup> Various chelating reagents have been examined as a component of the so-called 'TISAB' (total ionic strength adjustment buffer solution). Its performance is sometimes referred to the tolerance limit of aluminium because of its high affinity for fluoride and abundance in the environment.<sup>5,6</sup> However, a masking reagent suitable for one metal is not always efficient for another; metal ions have a wide variety of properties such as electric charge and ionic radius.

The potential response of a fluoride ISE has been studied in the presence of tetravalent metal ions from several points of view. First, Th<sup>IV</sup> was used as a titrant for the potentiometric determination of fluoride to form precipitates of ThF<sub>4</sub>.<sup>7</sup> The species formed in the titration were identified, the relevant equilibrium parameters (stability constants and solubility

products) evaluated, and optimum conditions established based on these quantities.<sup>8–11</sup> Both Zr<sup>IV</sup> and Hf<sup>IV</sup> form water-soluble complexes on reaction with fluoride; the stability constants were also determined using a fluoride ISE.<sup>12,13</sup> Second, the potential response of a fluoride ISE in 'fluoride ion-buffered solutions' was examined from a theoretical interest. The potentials correctly reflected the free fluoride concentrations down to  $1 \times 10^{-9}$  mol dm<sup>-3</sup> in equilibrium with an excess of Zr<sup>IV</sup> or Th<sup>IV</sup>.<sup>14,15</sup> This indicates the serious interference by these metal ions, the elimination of which has not been studied so far.

In a previous paper, several aminopolycarboxylates were examined for masking Zr<sup>IV</sup>, and diethylenetriamine-*N,N,N',N'',N'''*-pentaacetic acid (DTPA) was found to be excellent.<sup>16</sup> In this paper, the masking of other metal ions, viz., Hf<sup>IV</sup> and Th<sup>IV</sup>, was examined and suitable conditions were established for the determination of fluoride in the presence of these metal ions, including Zr<sup>IV</sup>.

## Experimental

### Reagents

A 1 g amount of hafnium(IV) chloride was dissolved in 10 cm<sup>3</sup> of 10 mol dm<sup>-3</sup> HClO<sub>4</sub>. The mixture was heated to expel HCl gas and diluted with 300 cm<sup>3</sup> of 1.4 mol dm<sup>-3</sup> HNO<sub>3</sub> to give a Hf<sup>IV</sup> stock solution. Thorium(IV) stock solution was prepared by dissolving Th(NO<sub>3</sub>)<sub>4</sub>·2H<sub>2</sub>O in  $1 \times 10^{-2}$  mol dm<sup>-3</sup> HNO<sub>3</sub>. Both stock solutions were standardized against ethylenediamine-*N,N,N',N'',N'''*-tetraacetic acid (EDTA) with Xylenol Orange. Other reagents were the same as described previously.<sup>16</sup>

The zirconium tetrafluoride (Morita Kagaku Kogyo), hafnium tetrafluoride (CERAC) and thorium tetrafluoride dihydrate (Katayama Kagaku Kogyo) used as samples were of technical grade.

### Measurement

The equipment used was the same as that described previously.<sup>16</sup> All the potentiometric measurements were performed at 25 °C and at an ionic strength of 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub>. The free fluoride concentration was determined using a fluoride ISE under various conditions. The recovery of fluoride,  $R = [F^-]/c_F$  ( $c_F$  = total concentration of fluoride), was used to evaluate the performance of the masking reagents.

### Recommended Procedure

A 0.05–0.1 g portion of the sample was placed in a platinum crucible and covered with 1 g of Na<sub>2</sub>CO<sub>3</sub>. The crucible was heated at 900 °C for 15 min. The cooled melt was digested

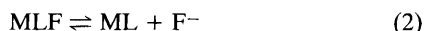
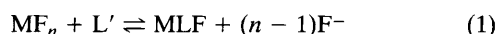
using 50 cm<sup>3</sup> of 0.04 mol dm<sup>-3</sup> DTPA. After dissolution, the pH of the solution was adjusted to 6 by the addition of 20 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> HNO<sub>3</sub>, and the solution was then diluted to 250 cm<sup>3</sup>. After a further 500-fold dilution, accompanied by adjustment of the ionic strength to 0.1 mol dm<sup>-3</sup> KNO<sub>3</sub>, the solution was subjected to potentiometry. Calibration graphs were constructed daily using two standard fluoride solutions at concentrations of  $1 \times 10^{-4}$  and  $1 \times 10^{-5}$  mol dm<sup>-3</sup>. The final concentrations were  $0.5 \times 10^{-5}$ – $2 \times 10^{-5}$  mol dm<sup>-3</sup> in F<sup>-</sup>,  $1 \times 10^{-6}$ – $5 \times 10^{-6}$  mol dm<sup>-3</sup> in metal ion,  $1.6 \times 10^{-5}$  mol dm<sup>-3</sup> in DTPA and  $0.8 \times 10^{-4}$  mol dm<sup>-3</sup> in carbonate buffer.

## Results and Discussion

### Comparison of Masking Reagents

Hafnium(IV) and Th<sup>IV</sup> seriously interfered with the determination of fluoride using an ISE. Some results for Hf<sup>IV</sup> are shown by the closed symbols in Fig. 1(a). Higher recovery was obtained by an increase in pH or by dilution of the solutions, but no conditions suitable for the determination of fluoride were found without masking reagents.

The effects of masking reagents, viz., EDTA, DTPA, *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CDTA) and triethylenetetramine-*N,N,N',N'',N''',N'''*-hexaacetic acid (TTHA), on *R* values were examined by varying the pH (from 3 to 7) and diluting the sample ( $c_F = 1 \times 10^{-5}$ – $1 \times 10^{-3}$  mol dm<sup>-3</sup>); the molar ratio of M:L:F was kept at 1:2:5. Some typical results for Hf<sup>IV</sup>–DTPA are shown by the open symbols in Fig. 1(a). Addition of masking reagents generally increases the recovery at any pH. As described previously,<sup>16</sup> two reactions are involved on this occasion (charges are omitted for clarity)



where MLF denotes a mixed ligand complex of a metal (M) with a masking reagent (L) and fluoride (F). As long as L is in excess over M, the equilibrium given by eqn. (1) is completely shifted to the right. As only one fluoride is left in the mixed ligand complex and the experimental conditions are chosen such that  $c_F = 5 \times c_M$ , at least 80% of the fluoride is recovered by this reaction. Any further increase in *R* from 80% depends on the equilibrium position of eqn. (2). The position is

governed only by the stability constant of the mixed ligand complex, irrespective of an excess concentration of L. Dilution of the sample [ $\square$  to  $\circ$  in Fig. 1(a)] is effective as pointed out previously.<sup>17</sup> The extremely low recovery found at pH values lower than 5 is due to protonation of the liberated fluoride. At higher pH levels, on the other hand, mixed-ligand complexes can react with hydroxide ions to expel fluoride by the following reaction:

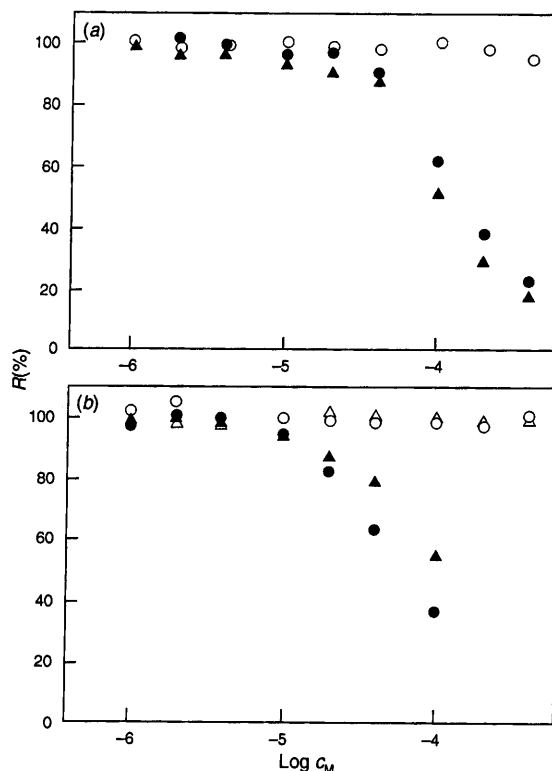
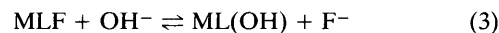


Fig. 2 Effect of higher concentrations of (a) Hf<sup>4+</sup> and (b) Th<sup>4+</sup> on the determination of fluoride. pH = 6; masking reagent:  $\circ$  and  $\triangle$ , DTPA (a) and TTHA (b);  $\bullet$  and  $\blacktriangle$ , EDTA (a) and (b);  $c_F$ /mol dm<sup>-3</sup>:  $\circ$  and  $\bullet$ ,  $1 \times 10^{-5}$ ;  $\triangle$  and  $\blacktriangle$ ,  $1 \times 10^{-4}$ .

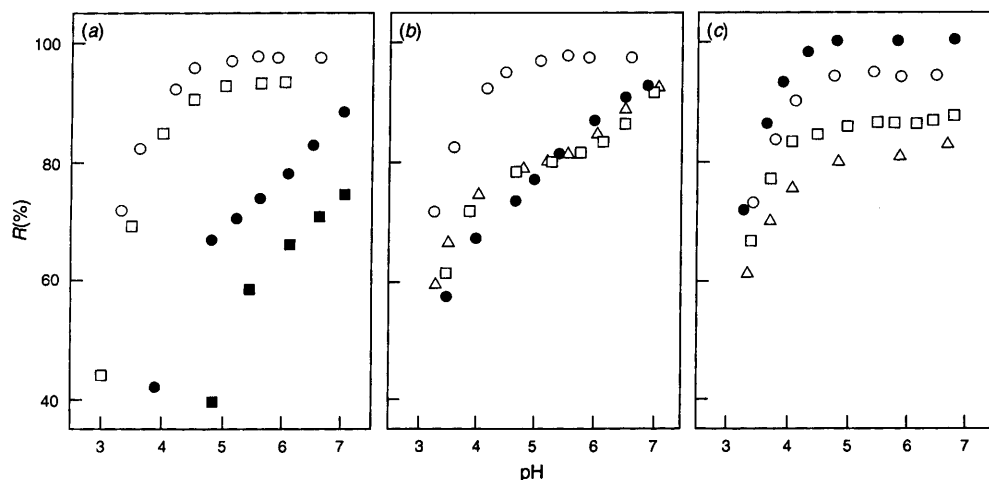


Fig. 1 Effects of masking reagent, pH and dilution on recovery of (a) F<sup>-</sup> in the presence of Hf<sup>4+</sup> and comparison of masking reagents for (b) Hf<sup>4+</sup> and (c) Th<sup>4+</sup>.  $c_M = c_F/5$ ;  $c_L = 2 \times c_M$ . (a)  $c_F$ /mol dm<sup>-3</sup>:  $\circ$  and  $\bullet$ ,  $1 \times 10^{-4}$ ;  $\square$  and  $\blacksquare$ ,  $1 \times 10^{-3}$ ; masking reagent:  $\bullet$  and  $\blacksquare$ , none;  $\circ$  and  $\square$ , DTPA. (b) and (c)  $c_F = 1 \times 10^{-4}$  mol dm<sup>-3</sup>; masking reagent:  $\circ$ , DTPA;  $\bullet$ , TTHA;  $\square$ , CDTA; and  $\triangle$ , EDTA.

This leads to an increase in the recovery, but the pH range available for the use of a fluoride ISE is limited to values lower than 6 because of the interference from hydroxide ion.

In masking  $\text{Hf}^{\text{IV}}$  [Fig. 1(b)], no plateaux in plots of  $R$  against pH were found for EDTA, CDTA and TTHA. These  $\text{Hf}^{\text{IV}}$  complexes have relatively high affinities for hydroxide as well as fluoride, so that an increase in  $R$  according to eqn. (3) starts at lower pH. Only DTPA gave a pH range for quantitative recovery of fluoride because the  $\text{Hf}$ -DTPA complex has a negligibly small affinity for fluoride.<sup>18</sup> Fluoride concentrations lower than  $1 \times 10^{-4} \text{ mol dm}^{-3}$  can be determined using DTPA at pH 5–6.5.

With  $\text{Th}^{\text{IV}}$  [Fig. 1(c)], however, plateaux were observed for all the masking reagents, which are attributable to the fact that Th complexes have relatively low affinities for hydroxide ion. TTHA is the best masking reagent as it has sufficient donor atoms to encircle  $\text{Th}^{\text{IV}}$ , which has a larger ionic radius (1.05 Å for  $\text{Th}^{\text{IV}}$ ; 0.84 Å for  $\text{Zr}^{\text{IV}}$ ; 0.83 Å for  $\text{Hf}^{\text{IV}}$ ). At pH 5–6.5,  $< 1 \times 10^{-4} \text{ mol dm}^{-3}$  fluoride can be determined using TTHA, and  $< 1 \times 10^{-5} \text{ mol dm}^{-3}$  fluoride using DTPA. Neither EDTA nor CDTA was suitable.

The interference from higher concentrations of  $\text{Hf}^{\text{IV}}$  or  $\text{Th}^{\text{IV}}$  was studied for the determination of fluoride at the  $1 \times 10^{-5}$  and  $1 \times 10^{-4} \text{ mol dm}^{-3}$  levels in the presence of these masking reagents. The results are shown in Fig. 2. When 95% was selected as a measure of quantitative detection by the fluoride ISE, Zr and Th up to a concentration of  $10^{-3.4} \text{ mol dm}^{-3}$  were effectively masked with DTPA and TTHA, respectively. Hence, at least a 4-fold metal concentration is tolerated for  $1 \times 10^{-4} \text{ mol dm}^{-3}$  fluoride and a 40-fold metal concentration for  $1 \times 10^{-5} \text{ mol dm}^{-3}$  fluoride. With EDTA, which was used in a conventional TISAB, the tolerable amounts were only  $1 \times 10^{-5} \text{ mol dm}^{-3}$  for Hf and  $10^{-5.5} \text{ mol dm}^{-3}$  for Th.

#### Dissolution of Fluoride From the Membrane in the Presence of Masking Reagents

In principle, the electroactive material of the fluoride ISE ( $\text{LaF}_3$ ) continues to dissolve into the sample solution during measurement. The rate, however, is extremely slow and the amount limited, so that the interference from the dissolved fluoride is negligible under common conditions. In this work, strong complexing reagents, which are also effective for  $\text{La}^{3+}$ , are used in relatively high concentrations. Possible enhancement of membrane dissolution was, therefore, assessed.

A fluoride ISE was soaked in a series of solutions (pH = 2–3; masking reagent:  $1 \times 10^{-4}$  and  $1 \times 10^{-5} \text{ mol dm}^{-3}$  EDTA, DTPA or TTHA). After 3 h, the pH was adjusted to 6 and the emf measured. The potentials obtained were below the detection limit. The concentration of dissolved fluoride

was thus estimated to be less than  $1 \times 10^{-7} \text{ mol dm}^{-3}$ , which does not interfere with the determination of fluoride at the  $1 \times 10^{-5} \text{ mol dm}^{-3}$  level.

#### Dissociation Rates of Fluoride From Metal Complexes

The rates of the reactions between fluoro complexes of  $\text{Hf}^{\text{IV}}$  or  $\text{Th}^{\text{IV}}$  and masking reagents to expel fluoride were qualitatively studied. Solutions of metal fluoro complexes ( $c_{\text{F}} = 1 \times 10^{-5}$  and  $1 \times 10^{-4} \text{ mol dm}^{-3}$ ;  $c_{\text{M}} = 1 \times 10^{-6}$ – $2.5 \times 10^{-5} \text{ mol dm}^{-3}$ ; pH = 2–3) were mixed with solutions of a masking reagent [ $c_{\text{L}} = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ; 2-morpholinoethanesulfonic acid buffer concentration/ $\text{mol dm}^{-3}$ : 0.65 (Hf), 0.1 (Th)] and the free fluoride concentration was monitored as a function of time. For comparison, a solution containing only buffer and no masking reagent was also examined.

Within 5 min after the addition of the masking reagent solution, quantitative recovery was achieved in each instance. In the absence of a masking reagent, recovery became constant within 10 min but was not quantitative. The substitution reactions of fluoride with masking reagents on these metal ions are rapid.

At a Th:F molar ratio close to 1:4 and at a moderate pH value,  $\text{ThF}_4$  is prone to precipitate. Once precipitates were formed, the reaction with the chelating reagents was extremely slow. Zirconium(IV) and  $\text{Hf}^{\text{IV}}$  do not form precipitates on reaction with fluoride in aqueous solution. Solid  $\text{ZrF}_4$  and  $\text{HfF}_4$ , on the other hand, react very slowly with masking reagents in suspended solution (at least several hours). Pre-treatment is required for solubilization of these materials.

#### Determination of Fluoride in Raw Materials of Fluoride Glasses

Raw materials of fluoride glasses (technical grade) and their mixtures in various ratios were analysed according to the recommended procedure (Table 1). Purities based on the fluoride content were 91.2% for  $\text{ZrF}_4$ , 95.3% for  $\text{HfF}_4$  and 100.5% for  $\text{ThF}_4 \cdot 2\text{H}_2\text{O}$ . The infrared spectra of  $\text{ZrF}_4$  and  $\text{HfF}_4$  showed an absorption band at about  $1640 \text{ cm}^{-1}$ , which was assigned to strongly adsorbed water molecules. The sample of  $\text{ZrF}_4$  was the same as that used previously<sup>16</sup> and the purity was 96.2%. Even in the presence of phosphorus pentoxide, these compounds slowly absorbed water.

Mixtures of the three compounds in various ratios (molar ratio = 2:1:1, 1:2:1 and 1:1:2) were also analysed using DTPA. The fluoride contents obtained agreed with the weighted average of the contents for the components (26.6% for 1:1:2, 28.6% for 1:2:1 and 31.0% for 2:1:1). Hence, fluoride can be determined in the presence of  $\text{Zr}^{\text{IV}}$ ,  $\text{Hf}^{\text{IV}}$  and  $\text{Th}^{\text{IV}}$  simultaneously, using the proposed method.

This study was supported by Grants-in-Aid for Science Research (Nos. 02640444 and 05640680) from the Ministry of Education, Science and Culture, Japan.

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**Table 1** Determination of fluoride in raw materials of fluoride glasses and their mixtures

Sample	Masking reagent	Fluoride (%)	
		Measured	Calculated*
$\text{ZrF}_4$	DTPA	40.9, 41.8	45.4
$\text{HfF}_4$	DTPA	28.3, 28.6	29.9
$\text{ThF}_4 \cdot 2\text{H}_2\text{O}$	TTHA	21.6, 22.1, 22.2, 22.7	22.1
	DTPA	22.0, 22.5	
1:1:2†	DTPA	26.9, 26.9	
1:2:1†	DTPA	27.2, 28.6, 28.7	
2:1:1†	DTPA	30.8, 31.2	

\* Calculated for the pure compound.

† Molar ratio of  $\text{ZrF}_4$ ,  $\text{HfF}_4$  and  $\text{ThF}_4 \cdot 2\text{H}_2\text{O}$ .

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Paper 4/02863E

Received May 16, 1994

Accepted July 27, 1994