

Masking of Zirconium(IV) in the Determination of Fluoride With an Ion-selective Electrode: Application to Zirconium(IV) Fluoride-based Glasses

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The performance of six chelating reagents [ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA); *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CDTA); *N'*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-triacetic acid (HEDTA); triethylenetetraamine-*N,N,N',N'',N''',N'''*-hexaacetic acid (TTHA); diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (DTPA); and citrate] has been studied for masking zirconium(IV) in the determination of fluoride with an ion-selective electrode. Citrate was not suitable because it produced a prolonged electrode response. Of the aminopolycarboxylates, DTPA has a much greater masking ability than the others. Using DTPA at pH 5–6, fluoride was successfully determined at a concentration of 1×10^{-5} mol dm⁻³ in the presence of up to 4×10^{-6} mol dm⁻³ zirconium(IV). The proposed method was applied to the analysis of a number of zirconium(IV) fluoride compounds and ZrF₄-based glasses after fusion with sodium carbonate.

Keywords: Fluoride determination; ion-selective electrode; fluoride glass; zirconium masking; diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid

In the last decade, heavy metal fluoride glasses, which generally contain zirconium(IV), hafnium(IV) or thorium(IV), have attracted much attention in relation to their potential use in long-distance fibre optics.^{1,2} In accordance with progress in this area, the determination of fluoride in the presence of these metal ions has increasingly been required; *e.g.*, chemical durability testing is essential to assess the utility of each fluoride glass, as the transparency of the glass in the middle infrared region (0.2–8 μ m) easily deteriorates as a result of attack from environmental water. To monitor the dissolution rate of a fluoride glass in an aqueous solution, a recent review³ recommends following the appearance of the dissolution products over a period of time, by analysis of the soaking solution, instead of following the loss in the mass of the glass. Metal components have been determined by various spectroscopic methods, and fluoride by potentiometry with a fluoride ion-selective electrode.^{4–9} Zirconium(IV), hafnium(IV) or thorium(IV) contained in these glasses has an extremely high affinity for fluoride^{10–15} and thus is expected to interfere seriously with the determination of fluoride. To eliminate the interference, commercially available TISAB (total ionic strength adjustment buffer solution), which contains citrate or *trans*-1,2-cyclohexanediamine-*N,N,N',N'*-tetraacetic acid (CDTA) as a masking reagent for metal ions,^{16,17} has been used. These reagents are effective for masking common metal ions such as Al³⁺, Fe³⁺ and Ca²⁺ but are not always suitable for metal ions in higher oxidation states. For example, Simmons and Simmons⁸ have observed that all the fluoride ions were not in the free form when CDTA was used as a masking reagent for zirconium(IV). No further work appears to have been undertaken since that report.

In previous papers,^{18–20} Yuchi and co-workers have studied the reaction of the fluoro complexes of trivalent metal ions with various masking reagents and found that mixed ligand complexes were generally present with a masking reagent and fluoride. Reagents forming less stable mixed ligand complexes are more efficient for the masking of a metal ion in the determination of fluoride by potentiometry using a fluoride ion-selective electrode. It has been found that ethylenediamine-*N,N,N',N'*-tetraacetic acid (EDTA) complexes of tetravalent metal ions also form stable mixed ligand complexes with fluoride.²¹

In the present paper, six chelating reagents [EDTA, CDTA, *N'*-(2-hydroxyethyl)ethylenediamine-*N,N,N'*-tri-

acetic acid (HEDTA), diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (DTPA), triethylenetetraamine-*N,N,N',N'',N''',N'''*-hexaacetic acid (TTHA) and citrate] have been examined for the determination of fluoride in the presence of zirconium(IV). Using DTPA as a masking reagent, fluoride was successfully determined in some zirconium fluoride compounds and ZrF₄-based glasses. As fluoride in these materials is prone to be replaced by oxygen-containing species such as OH⁻ and O²⁻ ions, these data will be complementary to the results for the determination of oxygen in fluoride glasses by charged particle activation analysis.²²

Experimental

Reagents

All the reagents used were of analytical-reagent grade. Potassium nitrate was recrystallized twice. Carbonate-free potassium hydroxide solution was prepared as described elsewhere.²³ Potassium fluoride was dried in a platinum crucible for 24 h at 110 °C. Fluoride solutions were stored in polyethylene containers. Zirconium(IV) stock solution was prepared by dissolving zirconium(IV) oxide nitrate, ZrO(NO₃)₂, in a 4 mol dm⁻³ nitric acid solution, which prevents the formation of polymeric hydrolysed species.²⁴ The concentration of zirconium(IV) was determined by titration with EDTA in 1 mol dm⁻³ HNO₃ at 90 °C using Xylenol Orange.

The zirconium tetrafluoride (Morita Kagaku Kogyo) and potassium hexafluorozirconate (Kanto Chemicals) used as samples were of technical grade.

Measurement

The equipment used was the same as that described previously.^{18–21} All the potentiometric measurements were performed at 25 °C and at an ionic strength of 0.1 mol dm⁻³ KNO₃.

The effects of pH and the concentrations of fluoride and zirconium(IV) on the electrode response were studied by utilizing various masking reagents; a series of solutions containing 2.5×10^{-6} – 2.5×10^{-4} mol dm⁻³ zirconium(IV), 1.25×10^{-5} – 1.25×10^{-3} mol dm⁻³ fluoride ion and 5×10^{-6} – 1×10^{-1} mol dm⁻³ masking reagent were titrated with 0.1 mol dm⁻³ potassium hydroxide. After each addition the

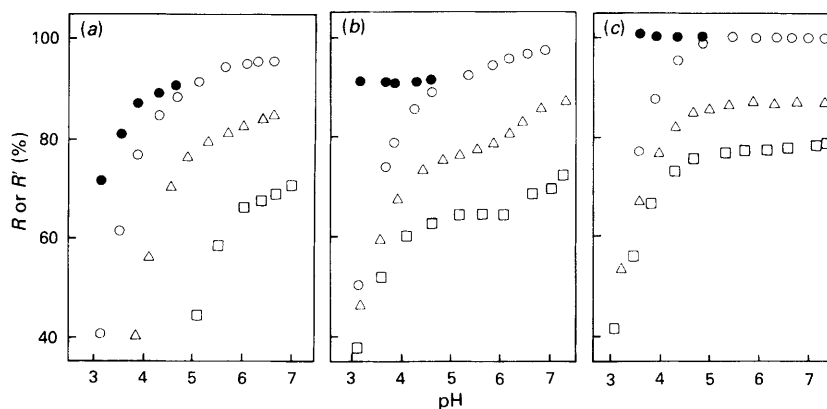


Fig. 1 R or R' (%) versus pH. Masking reagent: (a) none; (b) EDTA; and (c) DTPA. $c_F/\text{mol dm}^{-3}$: \square , 1.25×10^{-3} ; \triangle , 1.25×10^{-4} ; and \circ , \bullet , 1.25×10^{-5} . R : \square , \triangle and \circ ; and R' : \bullet . $c_F:c_{Zr} = 5$. $c_L:c_{Zr} = 2$

pF and pH were measured with a fluoride ion-selective electrode and a fluoride-resistant glass electrode. The recovery of fluoride, $R = [F^-]/c_F$ (c_F = total fluoride concentration), was calculated from the pF values. The recovery, taking the protonation of fluoride into account, R' , was also calculated by using the relevant constants and both pF and pH values¹⁸ (K is the formation constant in each instance).

$$R' = ([F^-] + [HF] + 2[HF_2^-])/c_F$$

$$= ([F^-] + K_{HF}[H^+][F^-] + 2K_{HF_2}K_{HF}[H^+][F^-]^2)/c_F$$

Recommended Procedure

A 0.05 g portion of the sample to be analysed is placed in a platinum crucible and covered with 1 g of Na_2CO_3 . The crucible is heated at 900 °C for 15 min. The cooled melt is digested with 60–70 cm³ of 1×10^{-2} mol dm⁻³ DTPA. After dissolution, 20 cm³ of 1 mol dm⁻³ HNO_3 are added, and the solution is diluted to 250 cm³. After a further 500-fold dilution the solution is analysed for fluoride.

Results and Discussion

Zirconium(IV) seriously interferes with the determination of fluoride as shown in Fig. 1(a). Although R increases with an increase in pH or with dilution of the sample, it does not reach 100% in the pH range suited to the use of the fluoride ion-selective electrodes. Addition of a masking reagent generally improves the recovery. The effects of pH and the concentrations of fluoride, zirconium(IV) and masking reagent were studied for each system (Figs. 1–3).

Effects of pH and Fluoride Concentration

In the presence of a masking reagent, R also increases with pH, steeply in an acidic medium and gradually in a neutral medium [Fig. 1(b) and (c)]. The increase in R at pH < 5 is due to the deprotonation of HF. As the formation of HF is negligible above pH 5, a plateau or an inflection point appears in the graph of R versus pH depending on the concentrations of fluoride and zirconium(IV).

At higher concentrations of fluoride and zirconium(IV), the formation of ZrF_n is mainly responsible for the interference in a slightly acidic medium, whereas at lower concentrations of fluoride and zirconium(IV) the interference is caused by ZrLF . [As the fully deprotonated ligands (L) used in this study have different electric charges, the net charges on the zirconium complexes are different to each other and therefore have been omitted for simplicity.]

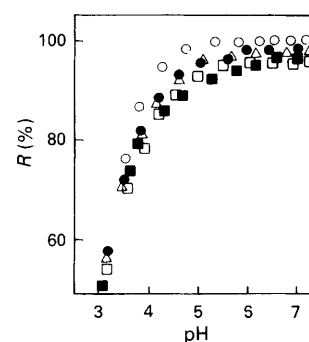
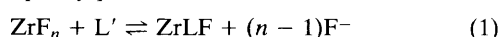
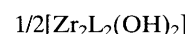


Fig. 2 Comparison of aminopolycarboxylates as masking reagents for Zr^{IV} . Masking reagent: \circ , DTPA; \bullet , TTHA; \triangle , HEDTA; \square , CDTA; and \blacksquare , EDTA. $c_F = 1.25 \times 10^{-5}$ mol dm⁻³. $c_{Zr} = 2.5 \times 10^{-6}$ mol dm⁻³. $c_L = 5 \times 10^{-6}$ mol dm⁻³

Both equilibria, particularly that given by equation (1), shift to the right by simple dilution of the sample. Hence, the sample should be diluted as much as possible within the dynamic range of the fluoride ion-selective electrodes. Such an effect has also been utilized to eliminate interference from aluminium.^{20,25}

The increase in R with pH found for the EDTA system [Fig. 1(b)] at pH > 6 is ascribed to the replacement of fluoride in the mixed ligand complexes by hydroxyl ions to form $\text{ZrL}(\text{OH})$ or $\text{Zr}_2\text{L}_2(\text{OH})_2$.



The R versus pH curves obtained agree well with those calculated using the relevant stability constants.^{21,26–28}

Comparison of Masking Reagents

Fig. 2 shows the masking abilities of aminopolycarboxylates for 0.25×10^{-5} mol dm⁻³ zirconium(IV) at a total fluoride concentration of 1.25×10^{-5} mol dm⁻³. Satisfactory recovery was obtained only with DTPA at pH > 5.

As R exceeds 80% for a sample with $c_F:c_{Zr} = 5$ in the neutral pH region (Fig. 2), the average number of fluoride ions bound to zirconium is less than 1. A higher concentration of an aminopolycarboxylate did not give a higher recovery. Hence, the equilibrium [equation (1)] is completely shifted to the right. In such solutions, the following relationships hold:

$$c_F = [\text{ZrLF}] + [\text{F}^-] \quad (4)$$

$$c_{Zr} = [\text{ZrL}] + [\text{ZrLF}] \quad (5)$$

$$K_{\text{ZrLF}}^F = [\text{ZrLF}]/[\text{ZrL}][\text{F}^-] \quad (6)$$

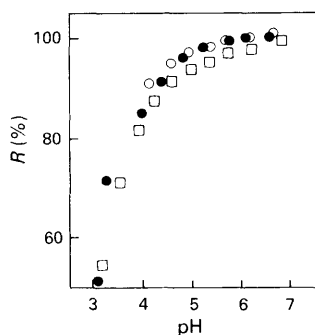


Fig. 3 Effect of citrate concentration on the recovery of fluoride. $c_F = 1.25 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{Zr} = 2.5 \times 10^{-6} \text{ mol dm}^{-3}$, $c_L/\text{mol dm}^{-3}$: \circ , 0.1; \bullet , 0.01; and \square , 0.001

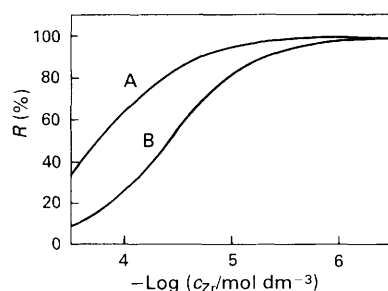


Fig. 4 Calculated recovery of fluoride versus $-\log c_{Zr}$ when masking zirconium with A, DTPA and B, EDTA. $c_F = 1.25 \times 10^{-5} \text{ mol dm}^{-3}$

For a solution containing known concentrations of fluoride and zirconium(IV), the recovery of fluoride can be calculated from these equations. The formation constant of the mixed ligand complex, K_{ZrLE}^F , for DTPA was found to be $10^{3.80}$, whereas that for EDTA has been previously reported²¹ to be $10^{4.52}$. Recovery of $1.25 \times 10^{-5} \text{ mol dm}^{-3}$ fluoride in the presence of various concentrations of zirconium(IV) was calculated and is shown in Fig. 4. When DTPA was used as a masking reagent, the tolerable amounts of zirconium(IV) for 99 and 98% recovery of fluoride are 2×10^{-6} and $4 \times 10^{-6} \text{ mol dm}^{-3}$, respectively. These values correspond to 16 and 32% as the molar ratio of zirconium(IV) to total fluoride and are sufficient for the analysis of fluoride glasses, because the molar ratios of these glasses are generally lower than 25%. Using EDTA, on the other hand, the tolerable amounts of zirconium(IV) are 4×10^{-7} and $8 \times 10^{-7} \text{ mol dm}^{-3}$ corresponding to only 3 and 6%, respectively. The potentially octadentate ligand, DTPA, may be the correct size to form a stable and coordination-saturated complex with zirconium(IV) similar to bis(nitrilotriacetate)zirconium,²⁹ and the resultant complex has a much lower affinity for fluoride ion.

For citrate (Fig. 3), a slight increase in recovery with an increase in the concentration of citrate from 0.001 to 0.1 mol dm^{-3} indicates a different reaction scheme. Even 0.1 mol dm^{-3} citrate solution, however, has a masking ability inferior to DTPA. Moreover, a higher concentration of citrate results in a prolonged response time of the fluoride ion-selective electrodes, which has been pointed out in relation to the masking of aluminium.^{30,31}

Pre-treatment

Dissolution of zirconium fluoride compounds is not easy; e.g., 0.004 g of finely powdered ZrF_4 suspended in 100 cm^3 of a $0.5 \times 10^{-3} \text{ mol dm}^{-3}$ DTPA solution stirred continuously required 7 h at pH 6–7 and 3 h at pH 3 to dissolve. Fusion with sodium carbonate was examined as a general method of pre-treatment for the dissolution of zirconium fluoride com-

Table 1 Determination of fluoride in samples containing zirconium

Sample	Fluoride (%)	
	Measured	Calculated
ZrF_4	43.5, 43.6, 44.0	45.5
K_2ZrF_6	37.6, 37.9, 38.3	40.2
ZB glass*	35.1, 35.1, 35.2	37.3
ZBLAN glass†	40.7, 41.2, 41.7	39.1

* $ZrF_4 : BaF_2 = 2 : 1$.

† $ZrF_4 : BaF_2 : LaF_3 : AlF_3 : NaF = 53 : 20 : 4 : 3 : 20$.

pounds. After fusion, even a fluoride glass sample could be dissolved in a DTPA solution. As fusion for 15, 30 or 60 min produced the same results, 15 min proved to be sufficient. It was necessary to treat the cooled melt with a DTPA solution before neutralization with nitric acid, in order to avoid prolonging the dissolution time. For samples containing relatively large amounts of zirconium, small amounts of a white precipitate, zirconium hydroxide or hydrated zirconium oxide, were formed during the neutralization of the DTPA solution with nitric acid. As potassium hexafluorozirconate was soluble in water, fluoride could be determined without fusion. When the same sample was pre-treated as described above, a white precipitate was formed but the analytical results were in good agreement with each other; thus the amount of fluoride in the precipitate is negligible. The addition of nitric acid results in a pH of about 6, which gradually increases with time owing to the evolution of CO_2 . Neither the precipitation of zirconium compounds nor the increase in pH interferes with the subsequent determination of fluoride. The solutions thus obtained can be kept for at least 1 week without any deterioration.

Determination of Fluoride in Samples Containing Zirconium

Fluoride in commercially available zirconium fluoride compounds of technical grade and in fluoride glasses was determined using the proposed procedure. Diethylenetriamine- N,N,N',N'',N''' -pentaacetic acid was effective for masking Ba^{2+} , La^{3+} and relatively small amounts of Al^{3+} . The results in Table 1 show a satisfactory reproducibility. Purities of commercial ZrF_4 and K_2ZrF_6 were 96.2 and 94.3%, respectively. The infrared absorption band at 1640 cm^{-1} suggests the presence of strongly adsorbed water molecules.²²

Prior separation of fluoride by conventional steam distillation was virtually impossible, although a recent paper³² describes a modified method, which is effective in the presence of zirconium(IV). As demonstrated above, potentiometry with a fluoride ion-selective electrode by using DTPA as a masking reagent is a more convenient and less time consuming method for the determination of fluoride in samples containing zirconium.

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