Journal of Fluorine Chemistry, 41 (1988) 25–32

ELIMINATION OF INTERFERENCE OF ALUMINUM ION BY A NOVEL RESIN PREPARED FROM DESFERRIOXAMINE AND POLYALLYLAMINE BEADS AND ITS APPLICATION TO THE DETERMINATION OF FLUORIDE ION

Y. OKABAYASHI*, M. IKEDA, T. NAKAGAWA, H. TANAKA

Faculty of Pharmaceutical Sciences,
Kyoto University, Kyoto 606 (Japan)

and M. CHIKUMA

Osaka University of Pharmaceutical Sciences,
Osaka 580 (Japan)

SUMMARY

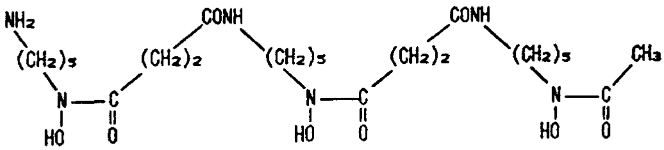
A novel functional resin for the selective adsorption of aluminum was prepared from desferrioxamine(DF) and polyallylamine(PAA) resin. The primary amino group of DF was conjugated with PAA by glutaraldehyde(GA). The resin was found to be effective for the elimination of interference caused by aluminum ion on the determination of fluoride ion. A new determination system for low levels of fluoride ion in the presence of aluminum ion was developed by the use of DF-PAA resin combined with anion exchange resin loaded with alizarin fluorine blue sulfonate; 3-[NN-di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone-5-sulfonate (AFBS) - lanthanum complex, which was a functional resin for selective collection of fluoride ion.

INTRODUCTION

Elimination of an interference caused by aluminum is still a difficult and important problem in the development of a system for the analysis of fluoride ion. We have prepared a novel

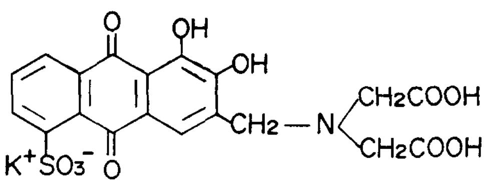
0022-1139/88/$3.50

functional resin which is able to adsorb aluminum ion selectively by the conjugation of desferrioxamine(DF), which chelates with aluminum selectively on polyallylamine beads(PAA).



Desferrioxamine (DF)

This paper briefly deals with the preparation of the resin(DF-PAA) and the determination of fluoride ion in the presence of aluminum by the use of this resin with a resin loaded with alizarin fluorine blue sulfonate; 3-[NN-di(carboxymethyl)aminomethyl]-1,2-dihydroxyanthraquinone-5-sulfonate (AFBS) - lanthanum complex which we have already developed for the selective collection of fluoride ion.



Alizarin fluorine blue sulfonate (AFBS)

EXPERIMENTAL

Reagents

(a) Desferrioxamine solution (0.02mol dm^{-3})

Desferrioxamine methanesulfonate (0.6568g) obtained from Ciba-Geigy was dissolved in water and diluted to 50ml.

(b) Polyallylamine beads

Polyallylamine beads (35-145 mesh), which is a new resin having only primary amino groups, were obtained from Nitto Boseki Co., LTD. [1,2]. The beads (2g) were shaken in 100ml of 1mol dm^{-3} sodium hydroxide for 1hour, filtered and washed with 1/15mol dm^{-3} phosphate buffer (pH 6.4) until the filtrate became neutral. The beads were filtered, washed with water and methanol, and dried.

Chemically pure reagents of glutaraldehyde(25% aqueous solution), aluminum standard solution (1000ppm) and fluoride standard solution (1000ppm) were purchased from Wako Pure Chemical Industries, LTD., Osaka, Japan. All other reagents used were of analytical-reagent grade. Deionized and distilled water was used throughout the experiment.

Apparatus

A Jasco 505 spectrophotometer with 1cm quartz cell was used for absorbance measurements. Concentrations of fluoride ion were measured with an Orion Model 94-09 fluoride ion selective electrode and an Orion Model 901 microprocessor ion analyzer.

Determination of aluminum ion

Aluminum ion was determined spectrophotometrically with chromazurol S [3]. To 1ml of sample solution (0.01-0.1mmol dm^{-3} aluminum(III) ion), 1ml of acetate buffer (pH 4.6), 2.6ml of water and 0.4ml of 0.165% chromazurol S were added in a plastic tube. The absorbance of the solution was measured at 567.5nm in a 1cm cell against a blank containing chromazurol S and acetate buffer.

Determination of desferrioxamine

Desferrioxamine (10^{-6} - 10^{-5}mol dm^{-3}) was analyzed spectrophotometrically by the formation of its iron(III) complex [4]. One ml of 0.02mol dm^{-3} iron(III) chloride (in 0.1mol dm^{-3} HCl), 1ml of 0.2mol dm^{-3} acetate buffer (pH 4.2) and 7.9ml of water were added to 0.1ml of sample solution. The solution was heated at 37^{o}C for 1h, cooled to room temperature and then the absorbance was read at 435nm against a blank solution containing iron(III) chloride and acetate buffer.

Conjugation of desferrioxamine to polyallylamine

After 2.5ml of 20mmol dm^{-3} DF was mixed with 5ml of 1/15mol dm^{-3} phosphate buffer (pH 6.4) and 0.5-2.0ml of 25% glutaraldehyde(GA) and incubated for 10min, 0.5g of PAA was added to the solution. The mixture was shaken for 4h at 37^{o}C. Then, unsaturated bonds of the product were reduced by adding 0.1g of sodium borohydride and shaking was continued for more than 1h at 37^{o}C. The resin was separated from the solution by filtration with a glass filter and washed with water. The unreacted primary amino groups of the resin were blocked with 0.7ml of formaldehyde (37%) in 1/15mol dm^{-3} phosphate buffer (pH6.4).

RESULTS and DISCUSSIONS

Masking of aluminium ion with desferrioxamine

Fig.1 shows the reaction rate curve of desferrioxamine(DF) and aluminum ion. DF was added to the solution containing fluoride ion and aluminum ion. Then, the concentration of fluoride ion, which was released from the complex of aluminum ion, was determined at scheduled time intervals. By this procedure, the complex of aluminum ion decomposed and released fluoride ion completely within 1h. Consequently, DF was found to be a better chelating agent than trans-1,2-cyclohexanediaminetetraacetic acid (CyDTA) or citric acid which have been used as masking agents for aluminum ion in the determination of fluoride ion by the use of ion selective electrode [5].

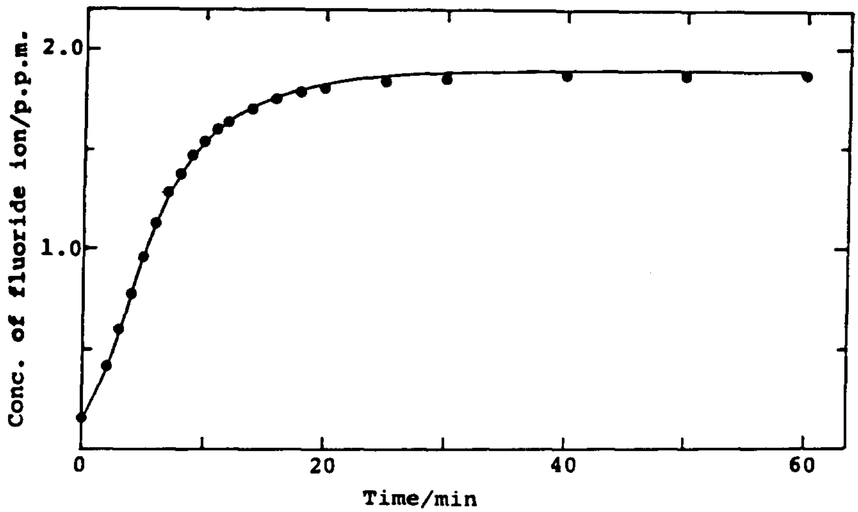


Fig. 1. Reaction rate curve.
Fluoride ion, 1.9p.p.m.; aluminum(III), 1mmol dm^{-3}; desferrioxamine, 1mmol dm^{-3}; acetate buffer, pH5.

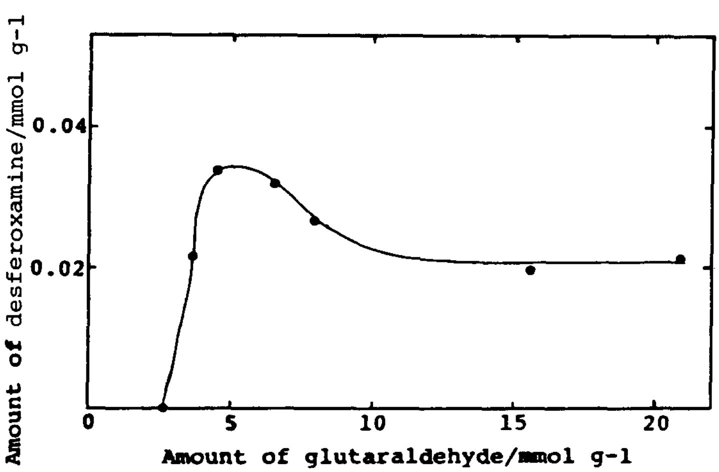


Fig. 2. Effect of amount of glutaraldehyde.
20mmol dm^{-3} desferrioxamine, 2.5ml; 1/15mol dm^{-3} phosphate buffer (pH6.4), 5ml; 25% glutaraldehyde, 0.5-4ml; polyallylamine, 0.5g; incubation time, 4h.

Conjugation of DF to PAA

The amount of GA was presumed to affect the amount of DF bound to PAA [6]. Fig. 2 shows the amount of DF bound to PAA for the different concentrations of GA added. When the amount of GA corresponded to the exchange capacity of PAA (15.0mmol g^{-1}), the amount of DF bound to PAA did not reach maximum. The reason for this result cannot be elucidated at present because of the complexity of the mechanism [7]. When 5mmol g^{-1} of GA was used, the amount of DF bound to PAA was found to be maximum.

Break-through curves for aluminum ion

Polypropylene columns were filled with DF-PAA prepared and PAA without DF, respectively, and the solutions containing aluminum ion and acetate buffer were passed through the columns. Fig. 3 shows that the adsorption capacity of DF-PAA was much higher than that of PAA without DF. From this result, we found

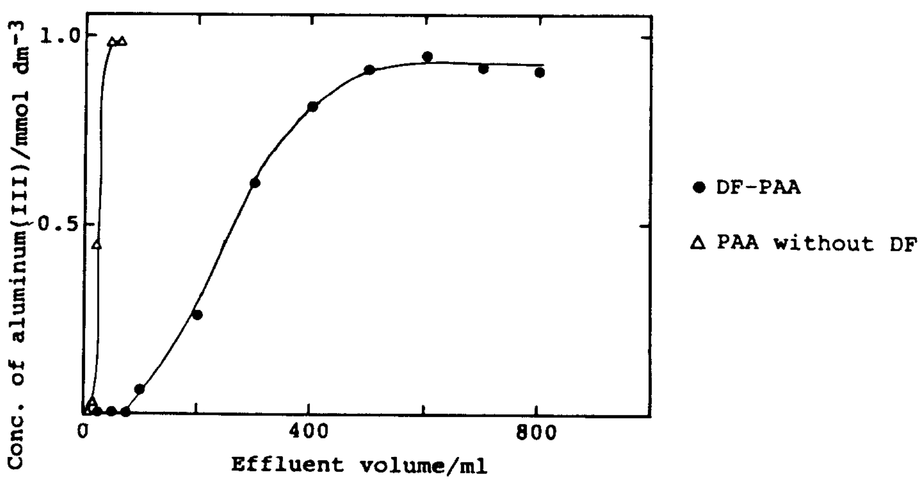


Fig. 3. Break-through curves for aluminum(III).
Aluminum(III), 1mmol dm^{-3}; 0.1mol dm^{-3} acetate - HCl buffer (pH5.34); temperature, 37°C; column, 10x15mm (0.2g).

that DF could form the complex with aluminum ion even when it was bound to resin. This result also shows that primary amino group of DF is independent of the complex of aluminum ion.

Elimination of aluminum ion

In order to investigate the ability of DF-PAA for the selective elimination of aluminum ion, DF-PAA was added to the solution containing aluminum ion and fluoride ion, the mixture was shaken for 2h and then the concentration of fluoride ion was determined by an ion selective electrode. We also examined the ability of Amberlite IRC-718, which is a chelating resin having iminodiacetic acid groups for selective elimination of aluminum ion. In the case of DF-PAA, the recovery of fluoride ion was about 90% when the concentration of aluminum ion was less than 0.1mmol dm^{-3} (Fig. 4). This recovery was much better than that of Amberlite IRC-718 and that obtained by direct determination

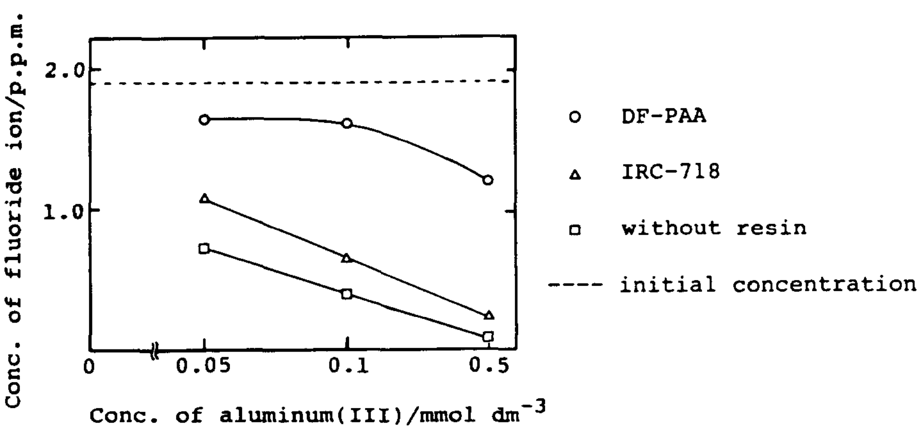


Fig. 4. Elimination of aluminum(III).
Aluminum(III), 0.05-0.5mmol dm^{-3}; fluoride ion, 0.1mmol dm^{-3}; 1mol dm^{-3} acetate buffer (pH6.36), 5ml; total volume, 50ml; resin, 0.2g; shaking time, 2h; temperature, 37°C.

without resin by ion selective electrode. Furthermore, recovery of fluoride ion was found to be satisfactory when DF-PAA was connected serially with the resin loaded with AFBS-La which we have reported as an effective functional resin for the selective collection of fluoride ion [8].

CONCLUSION

Desferrioxamine bound to polyallylamine could eliminate aluminum ion selectively. By the combined use of AFBS-La resin column and DF-PAA column, even low levels of fluoride ion in a solution containing aluminum ion could be determined.

REFERENCES

1 S. Harada and S. Hasegawa, Makromol. Chem. Rapid Commun., 5(1984) 27.

2 H. Serizawa, K. Shimizu and S. Harada, Polymer Preprints Japan, 33(1984) 85.

3 P. Pakalns, Anal. Chem., 32(1965) 57.

4 T. Emery and P. B. Hoffer, J. Nucl. Med., 21(1980) 935.

5 A. Yuchi, K. Ueda, H. Wada and G. Nakagawa, Anal. Chim. Acta., 186(1986) 313.

6 J. L. Marty, Appl. Microbiol. Biotechnol., 22(1985) 88.

7 F. M. Richard and J. R. Knowles, J. Mol. Biol., 37(1968) 231.

8 Y. Okabayashi, R. Oh, T. Nakagawa, M. Chikuma and H. Tanaka, The Analyst, in press.