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Short Communication

pH-Independent determination of aluminium as a cationic complex using capillary electrophoresis

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Abstract

The determination of aluminium as complex with desferrioxamine in presence of alkali and alkaline earth ions using indirect UV detection is shown. Desferrioxamine added to the analyte allows the pH-independent cationic determination of aluminium between pH 2 and 10 although the original aluminium is anionic.

1. Introduction

Aluminium has recently been recognised as a causative agent for dialysis encephalopathy and renal osteodystrophy [1,2]. This has led to the development of various analytical methods for the determination of aluminium such as graphite furnace atomic absorption spectroscopy (AAS) [3–7] or high-performance liquid chromatography (HPLC) [8]. In a recent work [9] aluminium was measured as a fluoro complex by using capillary electrophoresis (CE). In CE the detection is limited to a narrow pH range because the ionic form of aluminium strongly varies with the pH of the sample as shown in Fig. 1. Consequently the pH value of the sample has to be known. That means a greater volume of sample is needed to measure the pH so that the advantage of small samples is lost. In addition the introduction of an acidified sample is restricted on hydrostatic injection.

In aluminium-intoxicated haemodialysis desferrioxamine (DFO; 1-amino-6,17-dihydroxy-7,10,18,21-tetraoxo-27-(N-acetylhydroxyamino)-6,11,17,22-tetraazaheptaeicosane; Fig. 2) is used in chelation therapy [2,10]. Under the assumption that human serum can be seen as an aqueous system DFO was examined as a chelating agent in CE. According to Schwarzenbach and

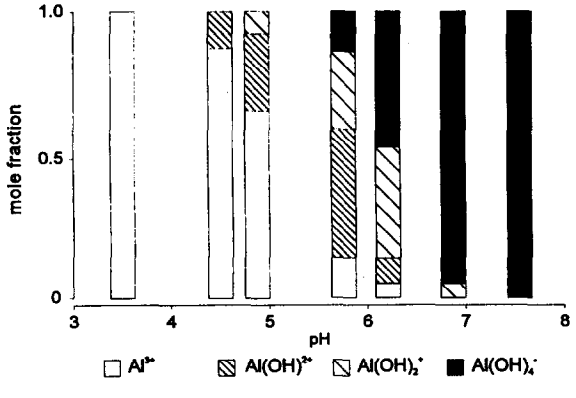

Fig. 1. Molecular forms of soluble aluminium hydroxide at different pH values. Redrawn from ref. 10.

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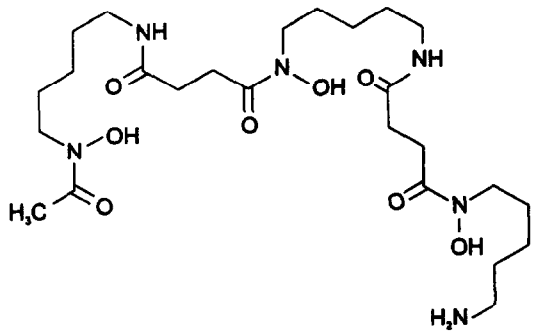

Fig. 2. Structural formula of desferrioxamine.

Schwarzenbach [11] DFO has four acidic protons, three from the hydroxamic acid group and one from the protonated terminal amino group —short formula $[H_4\text{–DFO}]^+$. It shows the following reaction

$$H_4\text{–DFO}^+ + Fe^{3+} \rightarrow 3H^+ + Fe[H\text{–DFO}]^+$$

The complex $Fe[H\text{–DFO}]^+$ is aprotic between pH 2 and 10. The analogous complex is assumed for aluminium.

2. Experimental

The capillary zone electrophoresis system has been described elsewhere [12] with the exception of the UV detector (Dionex, Sunnyvale, CA, USA). All solutions, electrolytes and standards were prepared using water purified with a Milli-Q system (Millipore, Eschborn, Germany). DFO was obtained from Ciba-Geigy (Wehr, Germany). All other reagents were of analytical-reagent grade from Merck (Darmstadt, Germany). Stock solutions (10 mmol/l) of each cation were used to prepare the sample solutions. Samples containing DFO were made by adding a stock solution (20 mmol/l DFO) after adjusting the pH with sodium hydroxide solution or hydrochloric acid and diluted to 1 mmol/l DFO. The capillary was rinsed for 5 min with 0.1 mol/l sodium hydroxide solution, water and electrolyte at the start of each day and for 2 min with electrolyte between all electrophoretic separations.

3. Results and discussion

4-Methylaminophenol sulphate (metol) was chosen as background electrolyte for the indirect UV detection of alkali and alkaline earth metal ions. Using this electrolyte aluminium can be determined as cationic Al^{3+} below pH 4. At higher pH values aluminium changes its ionic form and cannot be observed in an electrophoretic cation separation (Fig. 1). Although citric acid, hydroxyisobutyric acid and tartaric acid are useful complexing agents aluminium complexes of these agents could not be detected under the given CE conditions. The addition of DFO to the analyte allows the pH-independent cationic determination of aluminium between pH 2 and 10. DFO is an unsuitable additive for the electrolyte because it absorbs in the chosen range of UV and interacts with the fused-silica capillary wall. Because of the complex between aluminium and DFO has a higher absorbance than the background electrolyte $Al[H\text{–DFO}]^+$ was detected as a positive peak in simultaneous determination with other ions. DFO builds very stable complexes with Fe^{3+} but under the described experimental conditions a 100 μmol/l Fe^{3+} standard solution shows no peak as free ion as well as complex bound with DFO. Fluoride —also a well complexing agent for aluminium— was added in several concentrations between 10 μmol/l and 1 mmol/l before the addition of DFO. The formation of the Al–DFO complex was not disturbed.

The ionic mobility of the background electrolyte coion lies between those of the high-mobile alkali and alkaline earth and the low-mobile DFO–aluminium complex so that the peak symmetry is sufficient for all ions analysed in this study.

A representative collection of electropherograms (Fig. 3) shows the behaviour of peaks at different values of sample pH. In all measurements the pH value of the electrolyte was 5. The sample solution has a pH value of 4. In order to obtain a pH lower than in the standard solution hydrochloric acid was used. Furthermore a sodium hydroxide solution was added to raise the pH value. Therefore the peak area of sodium in Fig.

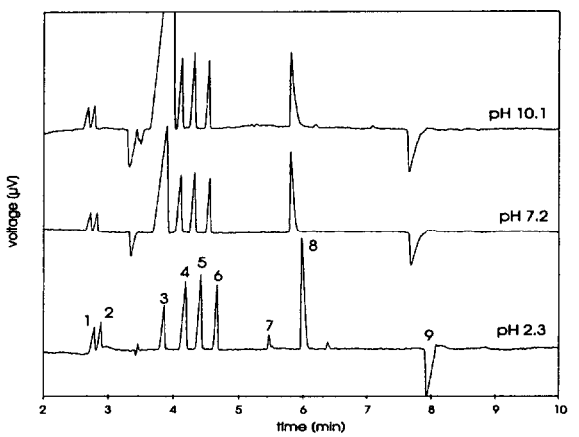

Fig. 3. Electropherograms of alkali, alkaline earth metal and aluminium ions at different sample pH values. Electrolyte 4 m*M* metol; fused-silica capillary 60 cm × 75 µm I.D.; voltage 30 kV; hydrostatic sample introduction (10 cm, 30 s). Peaks: 1 = caesium; 2 = potassium; 3 = sodium; 4 = calcium; 5 = magnesium; 6 = lithium; 7 = aluminium (Al^{3+}); 8 = cerium; 9 = aluminium ($Al[H-DFO]^{+}$); (each 100 µmol/l).

3 increases with increasing pH. At pH 2 a peak additional to the $Al[H-DFO]^{+}$ signal can be detected at the migration time of Al^{3+} in a system without DFO. At the increase of pH only the aluminium complex was detected. Reported complexation between DFO and calcium or magnesium [13] were not observed under CE conditions. The peak area of the aluminium complex shows pH independence in a range of pH 2 and 10 as shown in Fig. 4. Each data point

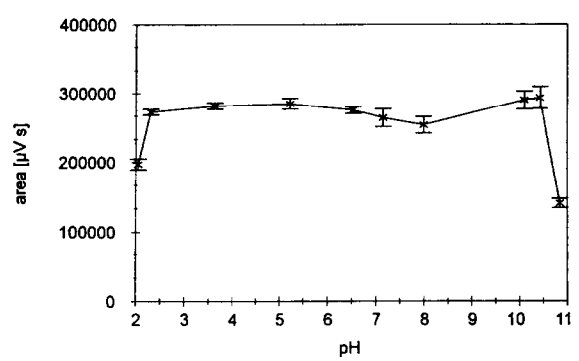

Fig. 4. Plot of the peak area of the desferrioxamine–aluminium complex (corresponding to 100 µmol/l Al^{3+}) *vs.* different values of sample pH.

in Fig. 4 is the mean value of five measurements with hydrostatic injection (10 cm, 30 s) of a 100 µmol/l Al standard solution. The relative standard deviation lies ranges between 0.02 and 0.05%. The precision of migration time amounts to 97.9%. The sample could be injected hydrostatically and electrokinetically. The peak areas show a linear dependence on concentration with coefficients of correlation of $r^2 = 0.994$ for electrokinetic injection (from 1 to 50 µmol/l) and $r^2 = 0.998$ for hydrostatic injection (from 25 to 500 µmol/l).

The measurement of aluminium with other complexing agents, as well as with DFO, limits of detection and determination in human serum will be reported in a following, more detailed publication.

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