Juliette Tria
Paul R. Haddad
Pavel N. Nesterenko

Australian Centre for Research on Separation Science (ACROSS), School of Chemistry, University of Tasmania, Hobart, Tasmania, Australia

Original Paper

Determination of aluminium using high performance chelation ion chromatography

The suitability of high performance chelation ion chromatography (HPCIC) using postcolumn reaction for the separation and determination of dissolved aluminium in complex samples was investigated. Use of a chelating ion-exchanger allowed for differentiation between kinetically labile and kinetically stable species of aluminium. Separation through a combination of chelation and cation-exchange was achieved using a 200 × 4.0 mm id column packed with particles of silica functionalised with iminodiacetic acid, with nitric acid – potassium chloride eluents. A temperature anomaly causing a five-fold increase in column efficiency for aluminium is believed to be a result of localised temperature effects in the particular type of instrument used. Postcolumn reagents investigated for the photometric detection included Tiron, Pyrocatechol Violet, Chrome Azurol S, and Eriochrome® Cyanine R. The lowest detection limit (2.7 μg/L for a 100 μL sample volume) was achieved using 0.25 mM Eriochrome Cyanine R in 0.2 M hexamine (pH 6.1) with 1 mM cetyltrimethylpyridium bromide (CTAB). The optimised HPCIC system was applied successfully to the quantification of labile aluminium in paper mill process water.

Keywords: Aluminium / High performance chelation ion chromatography / Postcolumn reaction

Received: January 25, 2008; revised: March 4, 2008; accepted: March 6, 2008

DOI 10.1002/jssc.200800046

1 Introduction

The ability to accurately and precisely quantify traces of aluminium is of significant interest to several disciplines. Aluminium is associated with toxicological and ecotoxicological effects, and these are now recognised universally. There is substantial evidence to suggest that abnormally high levels of aluminium are linked to conditions such as encephalopathy, bone disease and anaemia in humans [1, 2] and study continues into the involvement, if any, of aluminium as a cause of Alzheimer's disease [3, 4]. Additionally, aluminium is known to be toxic to many plants when solubilised in soil by acidic conditions [5], and abnormally elevated aluminium levels in waterways have been determined as the primary factor leading to fish extinction [1]. Aluminium is also of interest to oceanographers who use surface aluminium concentrations in open-ocean seawater as a tracer to fingerprint the location and magnitude of atmospheric dust deposition.

Multiple techniques, including graphite furnace-atomic absorption spectrometry [6], inductively coupled plasma atomic emission spectrometry [7, 8], inductively coupled plasma MS (ICP-MS) [7, 9 – 12], voltammetry [13], electron capture detection-GC [14], UV–Vis spectrophotometry [15] and fluorometry [16] have been applied for the determination of aluminium in various environmental samples. ICP-MS is perhaps one of the most favoured methods for aluminium analysis due to both the low detection limits possible (2.6 pmol/L to 0.4 nmol/L [9]) and its ability for multielement analysis. The major limitation of many of these techniques, particularly the spectroscopic methods, is the need for sample pretreatment. For the determination of aluminium in complex samples, preconcentration and/or clean up of the matrix is often required. Additionally, the information obtained

Correspondence: Professor Pavel N. Nesterenko, Australian Centre for Research on Separation Science (ACROSS), School of Chemistry, University of Tasmania, Hobart 7005, Tasmania, Australia
E-mail: pavel.nesterenko@utas.edu.au
Fax: +61-3-622628585

Abbreviations: CAS, Chrome Azurol S; **ECR,** Eriochrome Cyanine R; **HPCIC,** high performance chelation ion chromatography; **IC,** ion chromatography; **ICP-MS,** inductively coupled plasma MS; **IDAS,** iminodiacetic acid functionalised silica; **PCR,** postcolumn reaction; **PCV,** Pyrocatechol Violet; **PS-DVB,** polystyrene-divinylbenzene

via spectroscopic techniques is fairly limited and allows for only total solubilised aluminium to be determined, with no details of speciation. Consequently, chromatographic methods have become increasingly popular in recent years, due in part to the relative simplicity of such techniques, the wide scope of both separation/preconcentration materials and applicable detection methods and also the improved possibility for direct analysis of complex samples. Additionally, chromatography can provide information on the speciation of elements.

The use of ion chromatography (IC) for the quantification of aluminium was initially restricted to the determination of Al^{3+} [17]. However, the scope of this technique has since then been broadened to include separation and determination of multiple Al complexes (*e.g.* fluoro, oxalate, citrate) [18 – 21]. Both anion- and cation-exchange modes of IC may be utilised in order to determine positively or negatively charged species of aluminium [22]. The obvious restriction of using common ion-exchangers in IC separations is their high sensitivity to the presence of simple electrolytes (KCl, NH_4Cl, $CaCl_2$ and others) which are used frequently for the extraction of aluminium from samples such as soil, sediment and different plant materials [23]. Chelating ion exchangers are of particular interest for the separation and determination of aluminium as an alternative to traditional ion-exchange materials. They function by retaining metal ions according to the stability of the corresponding complexes and allow for the separation and preconcentration of aluminium in complex samples having a high content of alkali- and alkaline-earth metal salts.

The determination of aluminium takes into account three categories of species. These groups have been described as labile weakly bound monomeric (free aluminium, aluminium sulphate, fluoride and hydroxide complexes), nonlabile thermodynamically stable monomeric (complexes of aluminium with organic ligands) and kinetically inert thermodynamically stable polymeric type complexes and colloids [24]. Usually the differentiation of aluminium species is based on competitive complexation or/and acid reactivity [25]. Recently, competitive chelation with the chelating Chelex 100 resin (which carries iminodiacetic acid functional groups) has been used in a resin titration method proposed by Pesavento and coworkers [26]. So, another possible advantage of chelating ion-exchangers is their ability to discriminate between kinetically labile complexes and stable, inert complexes of aluminium, which provides additional information on the bioavailability and ecotoxicity of this element in natural samples.

High performance chelation ion chromatography (HPCIC), or other IC modes in which chelation is the dominant retention mechanism, offers several advantages over ion exchange separation [27, 28]. First, it allows for the possibility of using only one type of functionalised resin for both preconcentration and separation. This has obvious consequences in terms of the simplicity of a system for an application requiring both processes, since the same eluent can be used. Second, chelation acts in such a way as to convert all species of aluminium into uniform surface complexes. Whilst an ion-exchange chromatogram may show multiple peaks for largely unidentified aluminium species, a chromatogram using chelation will show only one or two; corresponding to total soluble and more strongly bound species. This is beneficial if full speciation of aluminium is not required.

There are few known attempts to use HPCIC for the separation and determination of aluminium. Jones and Schwedt [29] used different neutral polystyrenedivinylbenzene (PS-DVB) microspherical resins impregnated with Chrome Azurol S (CAS) dye, which has two salicylic acid groups in the molecule selective to aluminium. Isocratic separation of aluminium, indium and gallium was achieved on Benson BPI-10 resin with 1 M KNO_3 at pH 2.25 as the eluent. This separation was repeated on PS-DVB resin (Polymer Labs PRLP-S) [30] and a slightly different elution order (Al(III) < Ga(III) < In(III)) was observed. Two-step pH gradient elution from 2.2 to 1.0 in 1 M KNO_3 was used for the separation of aluminium, gallium, indium and iron (III) on a similar chromatographic column. Finally, this same HPCIC system was used for the determination of aluminium in seawater [31]. In all of these studies, photometric detection after postcolumn reaction (PCR) with 0.004% Pyrocatechol Violet (PCV) in 0.5 M hexamine adjusted to pH 6 was used.

The chromatographic behaviour of aluminium on Hamilton PRP-1 neutral PS-DVB resin dynamically modified with 4-chlorodipicolinic acid was investigated by Shaw *et al.* [32]. Aluminium was retained by this chelating substrate using an eluent comprising 1 M KNO_3 – 0.25 mM 4-chlorodipicolinic acid only when the eluent pH was higher than 2.0. The retention order Al(III) < La(III) < Lu(III) < Fe(III) < U(VI) was observed. The separation of aluminium and lead on a short (50 mm) column packed with aminocarboxylated polymethacrylate Bio-Rad HRLC-MA7C resin was also reported [33].

The most significant problem of the above-mentioned works was very poor column efficiency which is associated with the use of relatively coarse 7 – 10 μm polymer-based chelating resins and their slow kinetics of complexation with aluminium. This problem can potentially be overcome by the use of iminodiacetic acid functionalised silica (IDAS), which not only has a similar selectivity to Chelex 100 but also exhibits remarkable column efficiency in the separation of metal ions by HPCIC. The goal of the present investigation was to develop an HPCIC method suitable for the separation and determination of aluminium in complex samples, with possible application to the estimation of the labile fraction of soluble aluminium complexes in real samples.

2 Materials and methods

2.1 Apparatus

A Metrohm 844 UV/Vis Compact IC with built-in photodiode array UV/Vis detection was used for all analyses. The system allowed for the delivery of eluent at 0.2 – 2.5 mL/min and was set up with a column heater (up to 75°C) and a postcolumn reactor. Peristaltic pump tubing delivered the PCR reagent at a constant flow-rate of 0.36 mL/min. A sample loop of 20 μL was used unless stated otherwise. Two columns were used, namely a 250 × 4.0 mm id IonPac SCS-1 (Dionex, USA) packed with 4.5 μm poly(butadiene-maleic acid)-coated silica particles, and a 200 × 4 mm id column packed with 5 μm IDAS (JPP Chromatography, UK).

2.2 Reagents

All chemicals were of analytical-reagent grade. Potassium chloride solutions and all buffers underwent filtration (0.45 μm). KCl-HNO_3 eluent was prepared from stock 1 M KCl and 1 M HNO_3 solutions. Other eluents investigated were similarly prepared from stock solutions. Aluminium standards were prepared daily from a 1000 mg/L stock solution. All solutions were prepared using deionised water from a Milli-Q water purification system, Millipore (North Ryde, NSW, Australia). PCR reagents were Tiron (disodium salt of 4,5-dihydroxybenzenedisulphonic acid monohydrate), TCI (Taren Point, NSW, Australia); PCV, Aldrich (Castle Hill, NSW, Australia); CAS and Eriochrome® Cyanine R, both from Riedel-de Haën (Castle Hill, NSW, Australia).

2.3 Sample

A sample of paper mill effluent was obtained from the Boyer Mill, Hobart (Norske Skög, Boyer, Tasmania). The sample was filtered (0.45 μm) before analysis.

3 Results and discussion

The chemistry of aluminium in water is dominated by its predisposition to undergo hydrolysis, with the extent and type of hydroxy species formed being highly dependent on pH. The hydrolysis product of interest in the pH range of this study is the divalent hydroxy species ($Al(OH)^{2+}$), which forms at a pH of around 2.5 (Al 68.5 μM) (Puigdomenech, I., HYDRA-hydrochemical equilibrium-constant database, Version 18 February, 2004). The species distribution profile of the hydrolysis products can be altered by the addition of an electrolyte such as potassium chloride. Chloride can suppress the degree of hydrolysis due to the formation of its own complexes with aluminium, in particular $Al(Cl)^{2+}$, which is somewhat stable (log K −1.0) (Martell, A. E., Smith, R. M., NIST standard reference database 46, Version 8.0, 2004) and exists at low pH (< 4). The other common aluminium species in water include different complexes with carboxylic acids, polyphenols, fluoride and phosphate. The separation and identification of all species of aluminium is an extremely difficult task, so researchers usually determine only the labile soluble forms of aluminium after their conversion to a form suitable for detection as a single species. Such conversion of aluminium species can be performed by either addition of a suitable complexing reagent to the sample or by preconcentration on a chelating-resin, followed by elution with an inorganic acid.

3.1 Optimisation of separation conditions

Aluminium forms stable complexes with *O,O*-coordinating ligands, so carboxylic-type ion-exchangers can be used for separation of this cation by HPCIC. Two silica-based stationary phases with either a poly(butadiene-maleic acid) copolymer (PBDMA) surface layer or iminodiacetic acid functionalities were evaluated in terms of the peak profile of eluted aluminium. The peak of aluminium obtained with PBDMA was very broad and tailed, so the IDAS column was used for further experiments.

Eluents comprising KCl and HNO_3 were examined, using 0.3 mM Tiron in 1 M ammonium acetate as the PCR reagent. Experiments were carried out without column heating, unless specified otherwise.

3.1.1 Eluent pH and ionic strength

The retention of aluminium on IDAS should depend on both acidity and ionic strength of the KCl-HNO_3 eluent. The acidity of the eluent can affect separation in three ways. First, changing the acidity of the eluent affects the dissociation of the carboxyl moiety on the iminodiacetic acid functional group as can be appreciated by noting the applicable pK_a values of 2.59 (H_2L) and 1.85 (H_3L) (Martell, A. E., Smith, R. M., NIST standard reference database 46, Version 8.0, 2004). An increase in acidity reduces the number of negatively charged carboxyl groups through protonation which will, in turn, decrease electrostatic interactions. Second, conditional stability constants of the corresponding complexes between aluminium and IDA groups will also decrease. Both of these effects will result in a reduction in retention. Finally, a positive effect of increased acidity on retention is the reduction of hydrolysis of aluminium, which may also affect the separation efficiency. The ionic strength of the eluent governs the extent of electrostatic interactions with the ionised IDA groups. At high ionic strength these interactions are suppressed and chelation becomes the dominant separation mechanism [27]. However, since too high an ionic strength can lead to a decrease in column

efficiency due to increased viscosity, a balance between separation and column efficiency must be made.

With ionic strength maintained at 0.75 M KCl, the effect of acidity on the elution of aluminium from IDAS was investigated. A starting concentration of 30 mM nitric acid was chosen, based on conditions found to be successful for the elution of trivalent lanthanides from the same resin type [34]. Lower concentrations of nitric acid gave increased retention times, but led to a decrease of over 40 times in the number of theoretical plates obtained with the 30 mM nitric acid eluent. Despite the relatively low retention observed with 30 mM nitric acid, this concentration was chosen for subsequent experiments. This decision is supported in view of the superior column efficiency and the expectation of being able to increase retention by other means such as variation of flow rate.

Ionic strengths in the range of 0.1 – 0.75 M KCl were investigated, with the effects on retention time and column efficiency being illustrated in Fig. 1. Although a decrease of approximately 35 s in retention time resulted from increasing the ionic strength from 0.1 to 0.5 M, an increase in column efficiency of more than two-fold was accomplished. It should be noted that at concentrations higher than 0.5 M KCl, a decrease in column efficiency was observed due to viscosity effects. In view of this, 0.5 M KCl was chosen as the optimal eluent concentration. Different salts (potassium sulphate, ammonium sulphate and ammonium chloride) were also investigated but KCl was found to give best results.

In summary, the optimal eluent conditions were determined to be 0.5 M KCl and 30 mM HNO_3, which gave satisfactory peak shape, peak height and separation efficiency.

3.1.2 Column temperature

Temperature exerts considerable influence on separation in HPCIC. The thermodynamic effects of column temperature on retention can be described by the van't Hoff equation and these have been previously explained in detail elsewhere [27]. The impact of temperature change on retention is heavily reliant on the enthalpy of a system. For chromatographic systems in which chelation is the dominant mechanism, the enthalpy of reaction may be either exothermic or endothermic, so an increase in temperature may increase or decrease retention times. Additionally, the heats of sorption (ΔH) for chelating systems are generally significant in magnitude, so observable changes in retention in response to temperature change can be expected for HPCIC systems. Response of the system at temperatures in the range of 24 – 75°C was studied, with the latter temperature being the maximum possible for the Metrohm column heater. Figure 2 shows the dependence of retention of aluminium on column temperature. An increase in retention

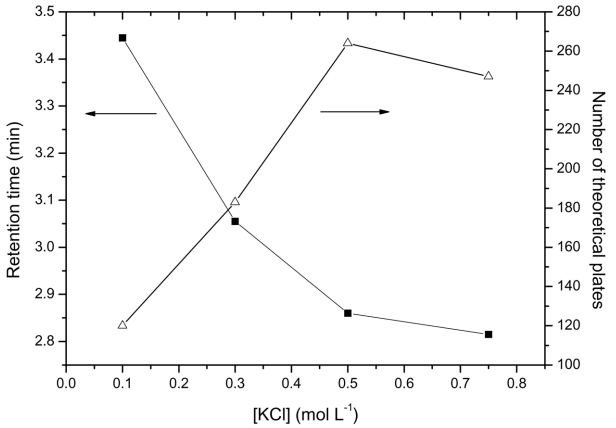

Figure 1. Dependence of retention time and column performance on concentration of KCl in the eluent. Experimental conditions: 15 cm IDA-silica column, 30 mM HNO_3, eluent delivery 0.8 mL/min.

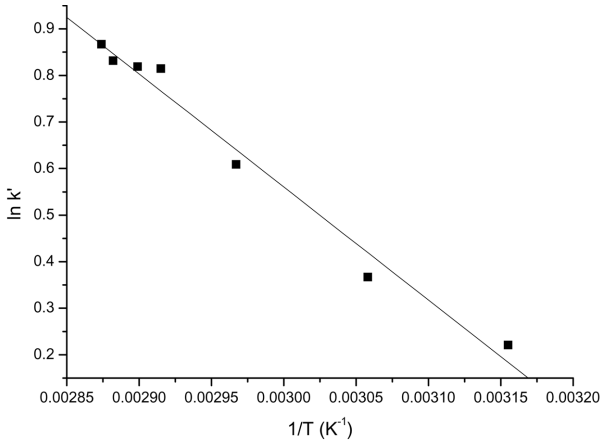

Figure 2. Dependence of retention of aluminium on column temperature. Experimental conditions: 15 cm IDA-silica column, 0.5 M KCl – 30 mM HNO_3 eluent delivered at 0.8 mL/min.

time of over 2.5 min was obtained by increasing the temperature from 24 to 75°C. This result agrees well with previous findings for 15 rare earth elements on IDA-silica [34]. The sorption enthalpy of aluminium with IDA was estimated to be 20.2 ± 1.3 kJ (mol K)$^{-1}$ from the slope of the plot in Fig. 2 and for such endothermic complexation reactions, higher temperatures shift the equilibrium in favour of complex formation and therefore increased retention.

Temperature also influences separation efficiency and it has been demonstrated that efficient HPCIC or IC separations of aluminium are possible only at column temperatures above 60°C [20, 29, 30]. The reason for this is the very slow interaction kinetics of the aluminium cation with chelating groups and the slow dissociation rates of complexed aluminium species normally present in real samples. Figure 3 shows column efficiency for an

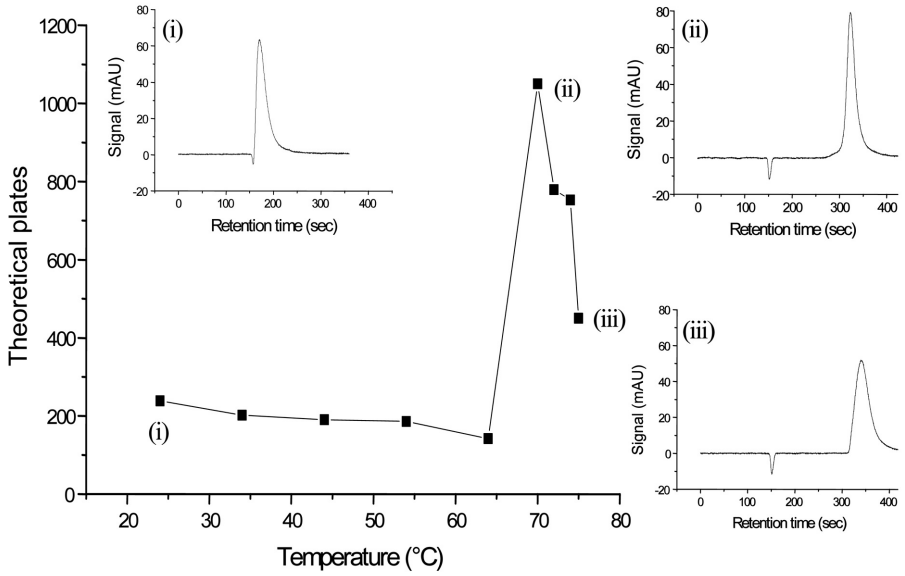

Figure 3. Dependence of column efficiency on column temperature. Experimental conditions: 15 cm IDA-silica column, 0.5 M KCl–30 mM HNO_3 eluent, delivered at 0.8 mL/min. (i) Peak corresponding to 24°C. (ii) Peak corresponding to 70°C. (iii) Peak corresponding to 75°C.

IDA-silica column and illustrates that between 64 and 70°C there is a sharp increase in efficiency, followed by a rapid decrease above 70°C. To the authors' knowledge, this type of dramatic response of column efficiency to column temperature has not been reported before and is believed to be specific to this particular chromatographic system. A possible explanation is the influence of localised temperature-induced viscosity changes on the shape of the sample band, resulting from the specific performance characteristics of the column heater and also the use of low thermal conductivity PEEK for the column and connecting tubing. This series of experiments was repeated using a water bath for heating the column and eluent and the strong dependence of efficiency on temperature shown in Fig. 3 was not observed. However, the highest efficiency achieved in this experiment was only 409 theoretical plates *per* column and for this reason the Metrohm column heater was preferred.

Further alterations to column conditions were made and included optimisation of eluent flow rate, additional length of chelating column and final adjustment of the concentration of acid and KCl in the eluent to 40 mM HNO_3 and 0.25 M, respectively. An eluent flow rate of 0.3 mL/min was selected since this provided sufficient retention of aluminium and a high column efficiency (>3000 theoretical plates).

3.2 Optimisation of PCR detection

PCR spectrophotometric detection is very common in HPCIC and IC [27], with Tiron and PCV being the reagents used most commonly for the determination of aluminium. The sensitivity of systems employing PCR for the detection of aluminium has been continually improved, with Jones *et al*. [35] reporting a detection limit of 1 μg/L (0.1 mL injection volume) using fluorescence detection of the 8-hydroxyquinoline-5-sulphonate–aluminium complex. An objective of the present study was to develop a system utilising a postcolumn reagent capable of such a detection limit using only photometric detection.

Tiron was chosen initially as the postcolumn reagent, based on its widespread use for the detection of aluminium. Initial working conditions for the Tiron postcolumn reagent were based on established conditions [18–20, 36] (Dionex Application Note AN 69, 1991), although none of these involved the inclusion of a surfactant in the reagent mixture. It has been shown that the addition of a surfactant to postcolumn reagents can often intensify the signal through interaction with micelles and in this study it was found that an addition of 0.5% w/v of Triton® X-100 to the PCR reagent resulted in a small improvement to both peak height and efficiency. A calibration plot of the optimised system showed good linearity between 0.2 and 20 mg/L (see Table 1 for regression data).

Alternate PCR reagents were examined in order to lower the LOD of the system. The results for the optimised Tiron system were compared to those obtained for PCV, CAS and Eriochrome Cyanine R (ECR), with this being the first reported use of the latter reagent for PCR determination of aluminium in a flow system. Column and eluent conditions were maintained as outlined above and concise optimisation of buffer and surfactant conditions and detection wavelength for each reagent

Table 1. Optimum conditions for PCR photometric detection of aluminium

Reagent	λ (nm)	Reagent mixture composition	LOD (μg/L)[a)]	Linearity[b)] range and regression data
Tiron	310	0.3 mM Tiron in 1 M ammonium acetate (pH 6.7) with 0.5% w/v Triton X-100	180	0.2 – 10 mg/L S = 361 (±3)
PCV	585	0.1 mM PCV in 0.2 M imidazole (pH 6.9) with 0.5% w/v Triton® X-100	28	c + 3.3 (±13)
ECR	580	0.25 mM ECR in 0.2 M hexamine (pH 6.1) with 1 mM CTAB	16	0.1 – 10 mg/L S = 6127 (±237)
CAS	590	0.26 mM CAS in 50 mM MES (pH 6.0) with 2% w/v Triton X-100	128	c + 1150 (±1200)

a) For a sample loop of 20 μL using standards prepared in deionised water.
b) S = signal (mAU · s); c = concentration (mg/L).

was undertaken. Whilst peak shape was similar between Tiron, PCV and ECR, their sensitivities for the detection of aluminium differed considerably (Table 1). It can be seen that ECR performed well with regard to both sensitivity and column efficiency, and optimal performance was observed using 0.25 mM ECR with 1 mM cetyltrimethylpyridium bromide (CTAB), buffered at pH 6.1 and with detection performed at 580 nm. When a 100 μL sample loop was used, the LOD (3σ) was 2.7 μg/L. Linear calibration was observed over the range of 0.0027 – 2 mg/L (regression data $S = 30514c$ (±1033) + 2362 (±1060) (n = 5), where S is peak area expressed in mAU · s).

3.3 Analysis of paper mill process water

A sample of paper mill whitewater was obtained from the Boyer Mill. This water is originally used to transport fibre onto the paper machine, at which stage it contains fibre from a variety of sources (softwood mechanical pulp, hardwood mechanical pulp and recycled fibre), clay and polymeric additives (used to aid in the retention and drainage of fibre on the paper machine). The whitewater is recirculated many times and the main source of any aluminium is the clay added in the papermaking process, or carry-over as $Al(OH)_3$ flocculent from the water treatment plant. The mill whitewater was analysed using the optimised ECR-system (using a 20 μL sample loop). Initial chromatograms of the sample showed two major peaks at 11.2 min (peak A) and 13.5 min (peak B), the second of which corresponded to free aluminium (as confirmed from spiking experiments). Acidification of the sample decreased the retention time for peak B but not for peak A, such that at pH 1.5 coelution of the two peaks occurred (Fig. 4b). ICP-MS analysis of the collected fraction of the effluent corresponding to peak A in Fig. 4b shows that this peak was also due to aluminium. This species appeared to be neutral, as its retention did not depend significantly on the pH of the eluent (see Fig. 5), and it was also stable under strongly acidic conditions. In addition, this species was evidently kinetically inert in view of the fact that it could be eluted as a discrete peak

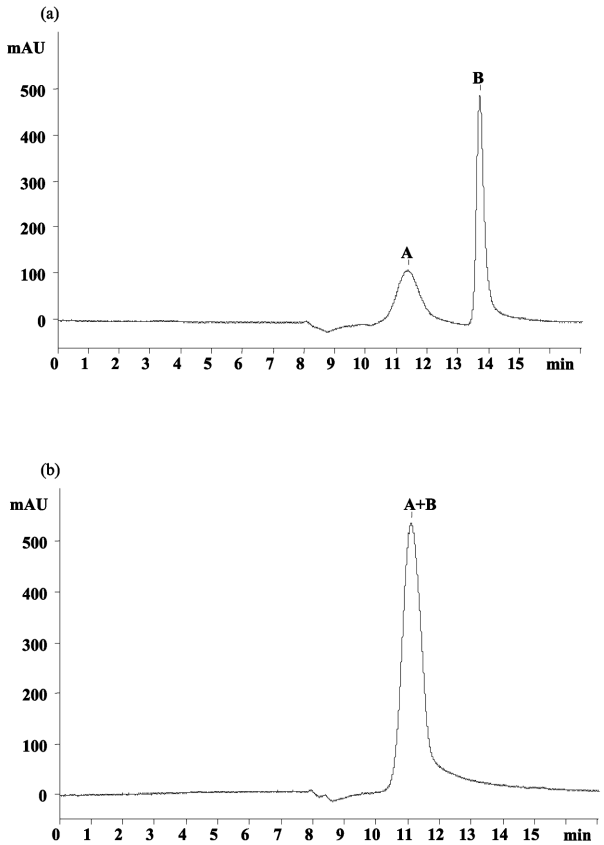

Figure 4. (a) Chromatogram of mill whitewater using optimised ECR-system (20 μL sample loop). Experimental conditions: 20 cm IDA-silica column at 71°C, 0.25 M KCl – 40 mM HNO_3 delivered at 0.3 mL/min. Sample was filtered and acidified to pH 4.8. (b) Chromatogram of mill whitewater using optimised ECR-system (20 μL sample loop). Experimental conditions: 20 cm IDA-silica column at 71°C, 0.25 M KCl – 40 mM HNO_3 delivered at 0.3 mL/min. Sample was filtered and acidified to pH 1 with HCl.

on the IDAS column, which has strongly complexing functional groups and is expected to behave similarly to Chelex 100 when used for resin titration speciation [26, 37]. However, this species still can react with ECR to produce a coloured, detectable complex.

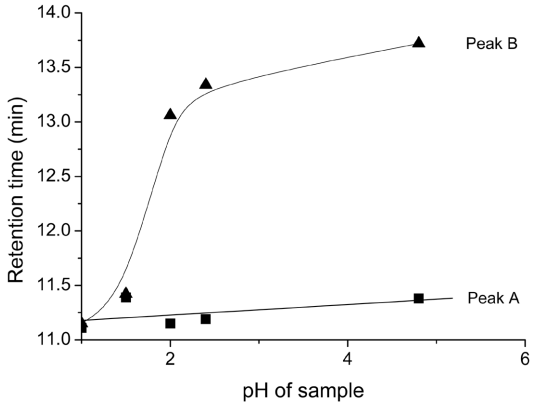

Figure 5. Effect of acidity of the sample on retention times of peaks A and B (see Fig. 4).

The exact identity of this early eluting species is not clear, but the aluminium must be bound very strongly by ligands in the sample in order to account for this shorter retention time. The existence of such stable complexes of aluminium has been reported elsewhere [26, 37 – 39], but again, the exact identity of the complexes has not been determined. It has been noted that the contribution of these strong ligands to the complexation of aluminium seems to be more important at low pH and when their concentration is in excess of aluminium [37]. In a sample of this nature it is believed that humic or fulvic acids may potentially form complexes of such high stability with aluminium, however this is merely speculative.

The concentration of the labile aluminium species in the process water (*i.e.* peak B) was determined to be 1.21 ± 0.05 mg/L ($n = 3$, $p = 0.95$). Standard addition of 0.5 mg/L of Al(III) to the sample gave a recovery of 99.3%. ICP-MS showed total dissolved aluminium in the unacidified sample to be 1.87 ± 0.03 mg/L ($n = 5$, $p = 0.95$). This value verifies the findings by our HPCIC method since the difference between the amounts measured by both techniques would have been due to the inert species of aluminium. The chromatographic peak area ratio for species B and A from the analysed sample is about 4.04, so the concentration of species A can be estimated from the PCR calibration plot (see Table 1) as 0.28 mg/L. In this case, the sum of concentrations of both species will give 1.21 + 0.28 = 1.49 mg/L. This is significantly less than the total concentration 1.87 mg/L of aluminium in the sample, as determined by ICP-MS, and it indirectly confirms the chemical inertness of specie A under conditions of PCR with ECR.

4 Concluding remarks

High performance chelation IC systems employing PCR were successfully developed and optimised for the determination of aluminium. Of the PCR reagents investigated, ECR, which was used for the first time for PCR detection of aluminium in a flow system, gave the best results, with an LOD of 2.7 μg/L obtained for a 100 μL sample loop. The innovative use of IDA functionalised silica for aluminium separation was successful and achieved peaks of good efficiency. Additionally, a unique dependence of column efficiency on temperature, believed to be specific for this system, was shown to exist. The optimised ECR system was successfully applied to the determination of aluminium in a sample of paper mill process water. The matrix of this sample was considered to be quite complex and two aluminium species were detected. The concentration of the labile species of aluminium in the sample was determined to be 1.21 mg/L.

The authors wish to thank Dr. Ashley Townsend, CSL, University of Tasmania, for the analysis of the paper mill process water by ICP-MS. The authors also acknowledge Dr. Des Richardson, Norske Skog, for the supply of the process water sample.

The authors declared no conflict of interest.

5 References

[1] Flaten, T. P., Alfrey, A. C., Birchall, J. D., Savory, J., Yokel, R. A., *J. Toxicol. Envron. Health* 1996, *48*, 527 – 541.

[2] Corain, B., Bombi, G. G., Tapparo, A., Perazzolo, M., Zatta, P., *Coord. Chem. Rev*. 1996, *149*, 11 – 22.

[3] Williams, R. J. P., *Coord. Chem. Rev*. 2002, *228*, 93 – 96.

[4] Solfrizzi, V., Colacicco, A. M., D'Introno, A., Capurso, C., Del Parigi, A., Capurso, S. A., Torres, F., Capurso, A., Panza, F., *J. Alzheimers Dis.* 2006, *10*, 303 – 330.

[5] Williams, R. J. P., *Coord. Chem. Rev*. 1996, *149*, 1 – 9.

[6] Orians, K. J., Bruland, K. W., *Earth Planet. Sci. Lett*. 1986, *78*, 397 – 410.

[7] Fairman, B., Sanz-Medel, A., Jones, P., Evans, E. H., *Analyst* 1998, *123*, 699 – 703.

[8] Hirayama, K., Sekine, T., Unohara, N., *Bunseki Kagaku* 1994, *43*, 1065 – 1070.

[9] Taylor, H. E., *Inductively Coupled Plasma-Mass Spectrometry – Practices and Techniques*, Academic Press, San Diego 2001.

[10] Jensen, D., Weiss, J., Rey, M. A., Pohl, C. A., *J. Chromatogr*. 1993, *640*, 65 – 71.

[11] Xia, L. B., Hu, B., Jiang, Z. C., Wu, Y. L., Li, L., Chen, R., *J. Anal. Atom. Spectrom*. 2005, *20*, 441 – 446.

[12] Prendez, M., Carrasco, M. A., *Envron. Geochem. Health* 2003, *25*, 347 – 363.

[13] Van den Berg, C. M. G., Murphy, K., Riley, J. P., *Anal. Chim. Acta* 1986, *188*, 177 – 185.

[14] Measures, C. I., Edmond, J. M., *Anal. Chem*. 1989, *61*, 544 – 547.

[15] Guray, T., Uysal, U. D., Gedikbey, T., Huseyinli, A. A., *Anal. Chim. Acta* 2005, *545*, 107 – 112.

[16] Manuel-Vez, M. P., Moreno, C., Gonzalez, D. J., Garcia-Vargas, M., *Anal. Chim. Acta* 1997, *355*, 157 – 161.

[17] Willett, I. R., *Soil Sci. Soc. Am. J*. 1989, *53*, 1385 – 1391.

[18] Motellier, S., Pitsch, H., *J. Chromatogr. A* 1994, *660*, 211 – 217.

[19] Busch, M., Seubert, A., *Fresenius J. Anal. Chem*. 2000, *366*, 351 – 355.

[20] Busch, M., Seubert, A., *Anal. Chim. Acta* 1999, *399*, 223 – 235.
[21] Hara, H., Kobayashi, H., Maeda, M., Ueno, A., Kobayashi, Y., *Anal. Chem*. 2001, *73*, 5590 – 5595.
[22] Happel, O., Seubert, A., *J. Chromatogr. A* 2006, *1108*, 68 – 75.
[23] Matus, P., Kubova, J., Bujdos, M., Medved', J., *Talanta* 2006, *70*, 996 – 1005.
[24] Sanzmedel, A., Fairman, B., *Mikrochim. Acta* 1992, *109*, 157 – 160.
[25] Driscoll, C. T., *Int. J. Environ. Anal. Chem.* 1984, *16*, 267 – 283.
[26] Alberti, G., D'Agostino, G., Palazzo, G., Biesuz, R., Pesavento, M., *J. Inorg. Biochem*. 2005, *99*, 1779 – 1787.
[27] Nesterenko, P. N., Jones, P., *J. Sep. Sci*. 2007, *30*, 1773 – 1793.
[28] Jones, P., Nesterenko, P. N., *J. Chromatogr. A*. 1997, *789*, 413 – 435.
[29] Jones, P., Schwedt, G., *J. Chromatogr*. 1989, *482*, 325 – 334.
[30] Challenger, O. J., Hill, S. J., Jones, P., *J. Chromatogr*. 1993, *639*, 197 – 205.
[31] Paull, B., Jones, P., *Chromatographia* 1996, *42*, 528 – 538.
[32] Shaw, M. J., Jones, P., Nesterenko, P. N., *J. Chromatogr. A* 2002, *953*, 141 – 150.
[33] Reiffenstuhl, S., Bonn, G., *J. Chromatogr*. 1989, *482*, 289 – 296.
[34] Nesterenko, P. N., Jones, P., *J. Chromatogr. A* 1998, *804*, 223 – 231.
[35] Jones, P., Ebdon, L., Williams, T., *Analyst* 1988, *113*, 641 – 644.
[36] Dean, J. R., *Analyst* 1989, *114*, 165 – 168.
[37] Pesavento, M., Biesuz, R., Palet, C., *Analyst* 1998, *123*, 1295 – 1301.
[38] Pesavento, M., Biesuz, R., Alberti, G., Sturini, M., *J. Sep. Sci.* 2003, *26*, 381 – 386.
[39] Pesavento, M., Biesuz, R., Dalla Riva, F., Alberti, G., *Polyhedron* 2002, *21*, 1343 – 1350.

