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Journal of Chromatography A, 910 (2001) 301–309

JOURNAL OF CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Sensitive and selective ion chromatographic method for the determination of trace beryllium in water samples

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Received 18 October 2000; received in revised form 30 November 2000; accepted 1 December 2000

Abstract

A selective and sensitive ion chromatographic method has been developed for the determination of beryllium in a number of water samples at low-μg/l concentrations. The separation was performed on a 250×4.0 mm I.D. iminodiacetic acid functionalised silica gel column. Chromatographed Be(II) was detected using visible detection at 590 nm following post-column reaction with chrome azurol S (CAS). The optimum separation and derivatisation conditions were studied in detail. The optimum eluent conditions were found to be 0.4 *M* KNO_3, adjusted to pH 2.5 using HNO_3, with optimum post-column detection being achieved using a solution containing 0.26 m*M* CAS, 2% Triton X-100, 50 m*M* 2-(*N*-morpholino)ethanesulfonic acid, pH 6.0. Under the above conditions, the concentration detection limit for Be(II) was found to be 3 μg/l in a standard solution and 4 μg/l in a typical tap water sample, using a 250 μl injection. The method was linear over the investigated range of 10 μg/l to 10 mg/l and highly reproducible. The method was successfully applied to a number of water samples of varying matrix complexity, including simulated seawater, and also to a natural freshwater certified reference material NIST 1640.

Keywords: Water analysis; Ion chromatography; Beryllium

1. Introduction

Beryllium (Be) is one of the most toxic non-radioactive elements to be found at trace levels in natural and industrial waste waters. Beryllium acts as an insidious carcinogenic poison, affecting cellular membranes and binding specific regulatory proteins in cells, with detectable excretory amounts present in urine for up to 10 years after initial exposure [1,2].

The monitoring of trace levels of Be(II) in natural waters is of interest as this indicates the extent of environmental pollution from anthropogenic sources such as the nuclear, aeronautical and metallurgical industries. Developed methods need to be both selective and sensitive as concentrations of Be(II) in natural and waste waters generally range from 0.1 to 500 μg/l, with concentrations exceeding 0.2 μg/l constituting an environmental hazard [3].

Over recent years numerous spectroscopic analytical techniques have been employed in the detection of Be(II) in water samples. These include spectrophotometric methods [4–6], spectrofluorimetric methods [7,8], flame atomic absorption spectroscopy (FAAS) [4,9], electrothermal atomic absorption spectroscopy (ET-AAS) [10–12], inductively coupled plasma atomic emission spectroscopy

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0021-9673/01/$ – see front matter
PII: S0021-9673(00)01242-5

(ICP-AES) [13], and inductively coupled plasma mass spectrometry (ICP-MS) [14]. Of these methods, ICP-MS is perhaps the most ideal due to the combination of a relative lack of susceptibility to matrix interferences, and sensitive mass detection, thus allowing most samples to be analysed without preconcentration or extraction steps. However, this method does require the purchase of highly complex and expensive instrumentation and so is not readily available to a great number of analytical laboratories. Of the remaining techniques mentioned above, spectroscopic interferences can be a problem when looking at real samples and so many published methods require the incorporation of some sort of separation/extraction methodology prior to analysis.

Such problems are not encountered when applying chromatographic methods to the determination of Be(II), particularly with the correct stationary phase selectivity. However, chromatographic methods for the determination of Be(II) are surprisingly few and far between considering the environmental interest in the monitoring of this toxic element. Several methods have been developed which are based upon either reversed-phase high-performance liquid chromatography (HPLC) of strongly absorbing Be(II) chelates [15,16], or cation-exchange chromatography [17–20]. Of the above, those methods based upon the pre-column formation of metal–ligand chelates have obvious disadvantages in terms of complex sample pretreatment and analysis time and so are not suited for routine monitoring. Those methods based upon cation-exchange chromatography are more suited to such an application but lack the desired stationary phase selectivity (or indeed detector selectivity if using conductivity) required for the analysis of anything other than relatively simple samples types such as drinking water and other low-ionic-strength samples.

Alternative complexing or chelating stationary phases for use in the ion chromatographic determination of Be(II) have recently been investigated by Voloschik et al. [3] and Shaw et al. [21]. Voloschik et al. used an iminodiacetic acid (IDA) functionalised silica gel column combined with a 5 m*M* HNO_3–2 m*M* dipicolinic acid eluent. Under these conditions Be(II) was well separated from common transition and heavy metals which were unretained, but eluted immediately after other alkaline-earth metals which meant the method was limited to samples with a relatively low Ca(II)/Mg(II) to Be(II) ratio, particularly as the detection method used was indirect conductivity. Most recently, Shaw et al. developed a method for the determination of Be(II) in a stream sediment which employed an aminomethylphosphonic acid functionalised silica gel stationary phase with a 1.0 *M* KNO_3, 0.5 *M* HNO_3 and 0.08 *M* ascorbic acid eluent. This substrate exhibited unique selectivity toward Be(II) based upon the coordination of the Be(II) ion with up to three O atoms of the methylphosphonic acid functional group. When used with the above strongly acidic eluent Be(II) could be separated from large excesses of common alkaline-earth and transition metal ions which were unretained. In this study by Shaw et al., post-column reaction detection was used for added selectivity. The post-column reagent solution used consisted of 0.008% chrome azurol S (CAS), 10 m*M* ethylenediaminetetraacetic acid (EDTA), 1.0 *M* hexamine (pH 6). However, the sensitivity of the method was reduced, due to the rather broad peak shape obtained for Be(II), which resulted from its strong affinity for the stationary phase. A detection limit of 35 μg/l was obtained for Be(II) in stream sediment digest.

The following paper details the development of a ion chromatographic method based upon the use of an IDA functionalised silica gel column with a high-ionic-strength eluent for the selective determination of trace Be(II) in various water samples. Development of the eluent conditions required for optimal selectivity when analysing complex natural and waste water matrices has been carried out, coupled with further development of sensitive post-column reaction detection. The final method was applied to the analysis of spiked potable and natural water samples, including simulated seawater, and a certified reference freshwater sample (NIST 1640).

2. Experimental

2.1. Instrumentation

A Dionex Model GPM2 gradient pump module (Sunnyvale, CA, USA) was used to deliver the eluent at 1.0 ml/min. A manual sample injection valve, Model 7125 (Rheodyne, Cotati, CA, USA), fitted

with a 100- or 250-μl injection loop, was used for sample introduction. The dimensions of the IDA-silica gel analytical column used were 250×4.0 mm I.D., with an 8 μm average particle size (Bio-ChemMack, Moscow, Russia). A pressure-driven Dionex reagent delivery module was used for introduction of the post-column reagent solution at 1.5 ml/min, which was mixed with the eluent using a 0.5 m×0.3 mm I.D. polyether ether ketone (PEEK) reaction coil. A Model SPD-6AV Shimadzu UV–Vis detector (Kyoto, Japan) was used at 590 nm to monitor the resultant chromatograms. These were recorded using Dionex A1450 chromatographic software.

2.2. Reagents

The eluent and post-column reagent (PCR) were prepared using deionised water from a Millipore Milli-Q water purification system (Bedford, MA, USA). CAS 65% sodium salt, 2-(*N*-morpholino)ethanesulfonic acid (MES) and Triton X-100 were purchased from Sigma–Aldrich (Gillingham, UK) and used without further purification. Potassium nitrate was obtained from Merck (Darmstadt, Germany). Final eluent conditions for the analysis of samples were 0.4 *M* KNO_3, adjusted to pH 2.5 using dilute HNO_3. The post-column reagent solution was 0.26 m*M* CAS, 2% Triton X-100, 50 m*M* MES, adjusted to pH 6.0 using dilute NaOH (after mixing of the eluent and PCR, the final solution pH at the detector was 5.9). All solutions were filtered through a 0.45-μm filter and degassed using sonication. Low-level standard solutions were generally prepared freshly each day from stock solutions (1000 mg/l), stored in PTFE containers and acidified using dilute nitric acid.

3. Results and discussion

3.1. Stationary phase selectivity

The use of chelating stationary phases for the high-performance separation of metal ions has been extensively investigated over the past 10 years and a number of comprehensive reviews have been compiled on the technique known as ‘‘chelation ion chromatography’’ [22–24]. Retention of metal ions on chelating stationary phases is dependent upon the conditional stability constants of the metal ion and the immobilised ligand, which are governed by the nature of the immobilised ligand, namely the number, position and type of coordination sites. As mentioned previously, the aminomethylphosphonic acid functionalised chelating stationary phase used by Shaw et al. [21], coordinates with the Be(II) ion through two or three O donator atoms. IDA, as used here and previously by Voloschik et al. [3] exhibits a lesser affinity for Be(II), coordinating with the metal ion though single N and O donator atoms. This means that when using a simple low-ionic-strength non-complexing eluent the column exhibits similar selectivity for Be(II) as for other alkaline-earth metal ions. This was shown by Voloschik et al., who, with a 7 m*M* HNO_3 eluent, obtained retention times of between 4 and 6 min for five alkaline-earth metal ions [Mg(II), Ca(II), Sr(II), Ba(II), Be(II)], and retention times between 5 and 8 min when the eluent contained 2 m*M* dipicolinic acid.

In recent work we have shown how retention of the alkaline-earth metals Mg(II), Ca(II), Sr(II) and Ba(II) on IDA functionalised silica gel was based upon a mixed mode retention mechanism of surface complexation and simple ion exchange [25]. It was shown how exploitation of this dual retention mechanism, through control of eluent pH and ionic strength, could result in large individual changes in selectivity for the alkaline-earth metal ions, Ca(II), Mg(II), Ba(II) and Sr(II). Using differing eluent combinations of ionic strength and pH, the above metals could be baseline separated in three different retention orders. In this current study, it was once again important to understand how eluent ionic strength and pH altered selectivity for Be(II), as this would provide information on the exact mechanism responsible for retention.

It is known that of the alkaline-earth metals, Be(II) is the most weakly retained when ion exchange alone is responsible for retention [17–20]. Therefore, it was expected that on the IDA-silica column, retention of Be(II) would be predominantly due to surface complexation and so less affected by eluent ionic strength than the above metals. Fig. 1 shows a plot of the log of the capacity factor, k', against log [eluent] for both Be(II) and the remain-

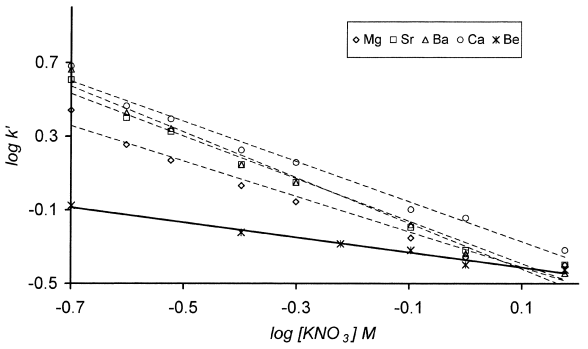


Fig. 1. Plot of log of the capacity factor, k', against log [KNO_3] for Be(II) at pH 2.5 and Mg(II), Sr(II), Ba(II), Ca(II) at pH 4.2.

ing alkaline-earth metals, using KNO_3 as the ionic strength modifier. The data for Be(II) was obtained using an eluent pH of 2.5. The data for the remaining alkaline-earth metals was obtained using a pH of 4.2 [as Mg(II), Ca(II), Sr(II) and Ba(II) were unretained at pH 2.5, and Be(II) was completely retained at pH >3]. From the graph it can be seen that Mg(II), Ca(II), Sr(II) and Ba(II) showed a greater reduction in capacity factor as a function of eluent ionic strength than Be(II), corresponding to ion exchange playing a more significant role in their retention. This is as expected, as at pH 4.2, one carboxylic acid of the IDA is almost fully dissociated (pK_{a1} value for IDA is approx. 2.6 [26]), therefore the stationary phase has the properties of a weak cation exchanger. However, at pH 2.5 the ion-exchange capacity of the stationary phase is greatly reduced, which together with the lower affinity of Be(II) for simple cation exchangers, indicates that Be(II) is predominantly being retained through surface complexation. Comparison of the linear regression slopes for the two sets of data clearly illustrate this difference in analyte ion retention mechanism, for Mg(II), Ca(II), Sr(II) and Ba(II), slopes range from -1.20 to -1.38, for Be(II) the slope is only -0.37, which in practical terms corresponds to a small reduction in retention time from 4 min with a 0.4 *M* KNO_3 eluent, to 3.5 min with a 1.5 *M* KNO_3 eluent. This high selectivity for Be(II) makes the IDA-silica column ideal for the determination of the metal ion in high-ionic-strength samples (see Section 3.3), which is indeed one of the main advantages of chelation ion chromatography in general. Thus, for the remainder of this study, 0.4 *M* KNO_3 was used as the eluent, as this was a sufficiently high enough concentration to suppress any retention due to ion exchange for both Be(II) and other alkaline-earth metals, and also resulted in an ideal retention time for Be(II) of between 4 and 5 min (pH 2.5).

The effects of eluent pH and column temperature were also studied. Fig. 2 shows the effects upon retention of Be(II) of (A) increasing eluent pH and (B) eluent temperature. Both sets of results were typical of surface chelation being the dominant retention mechanism, although retention through simple ion exchange would also increase with an increase in eluent pH, due to an increase in the concentration of deprotonated carboxylate groups.

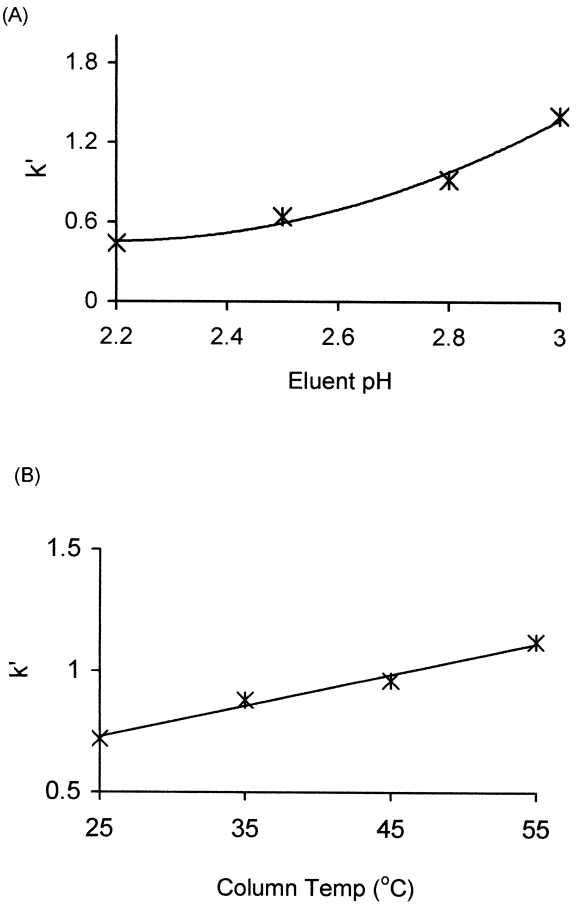


Fig. 2. Effects upon retention of Be(II) of (A) increasing eluent pH (other conditions: 0.4 *M* KNO_3) and (B) eluent temperature (other conditions: 0.4 *M* KNO_3, pH 2.5).

An increase in eluent pH effectively results in an increase in the conditional stability constants (K'_{stab}) for the Be(II)–IDA complex. Therefore, large increases in retention over relatively small changes in pH are typical. Here the peak shape for Be(II) also showed signs of rapidly broadening as the pH was increased above 3. This is again typical of surface chelation and is thought to be due to the relatively slow kinetics of complexation compared to those of ion-exchange, particularly if the stability constants for the chelate are high [23]. An additional factor to consider here is the formation of $Be(OH)^+$ ions at pH above 3, which could also play a role in peak broadening. This however was not a significant problem when using an eluent at pH<3 and so an eluent pH of 2.5 with 0.4 *M* KNO_3 was considered optimum.

Fig. 2B shows the effect of temperature upon the retention of Be(II), investigated using the above eluent. As the temperature of the column was increased from 25 to 55°C, the retention time of Be(II) also increased. This effect, which as mentioned above, is typical of complexation, has been convincingly explained by Jones and Nesterenko [23]. They stated that as the ''chelate effect'' was predominantly an entropy effect, surface complexation would result in a positive increase in entropy and so the change in Gibb's free energy with temperature would be negative. If temperature was increased, the change in Gibb's free energy would become even more negative and so the equilibrium constant for the complex being formed would become bigger, hence an increase in retention. Jones and Nesterenko state that with this in mind, if complexation was purely responsible for retention, an increase in temperature should result in an increase in retention. Therefore, from results obtained here we can again conclude that the retention of Be(II) was likely to be predominantly due to surface chelation. However, despite the above effect, temperature did not noticeably improve peak efficiency or other method performance indicators and so for simplicity reasons was neglected for the remainder of this study.

3.2. Post-column reaction detection

For improved selectivity and sensitivity in the chromatographic determination of metal ions, UV–Vis detection based on post-column reaction is often used. In their recent study, Shaw et al. [21] had shown CAS to be a sensitive reagent for the determination of Be(II). CAS is also a readily available and inexpensive reagent, and was therefore again employed in this work. A further advantage to using this reagent was that under the conditions detailed below, CAS did not produce a significant detector response for matrix metals such as alkali and alkaline-earth metal ions, which are likely to be present in excess in most natural, industrial and potable water samples.

Optimisation of the post-column reagent conditions involved investigating the effect of CAS concentration, pH and addition of the surfactant, Triton X-100. From it's visible spectrum it was clear that the Be(II)–CAS (1:1) complex absorbed strongly over a broad region between 560 and 610 nm. Injections of a 2 mg/l Be(II) standard solution at 10-nm intervals between the above two wavelengths revealed 590 nm to be the optimum wavelength in terms of peak signal-to-noise ratio.

The effect of varying the CAS concentration over the range 0.065 to 0.65 m*M*, had a great influence on the peak height of Be(II). Increasing the concentration of CAS initially led to an increase in the peak height for Be(II). However, as the CAS concentration approached 0.65 m*M*, the peak height of Be(II) began to level off and the background absorbance was substantially increased, resulting in a decreased signal-to-noise ratio. From the above results 0.26 m*M* CAS was found to be most appropriate.

Post-column reagent pH was investigated using repeat injections of a standard solution over the pH range of 4–7.5. On the basis of signal-to-noise ratio a pH of 6.0 was found to be most sensitive. MES at a concentration of 50 m*M* was used to buffer the post-column reagent to pH 6.0, which when combined with an eluent composed of 0.4 *M* KNO_3 at pH 2.5, resulted in a final pH of 5.9.

Finally, the effect of adding the surfactant Triton X-100 to the post-column reagent solution over the concentration range 0–4% was investigated. Triton X-100 has been shown previously to be an ideal surface active agent in such colour-development reactions, as it improves the solubilisation, dispersion

and stabilisation of the metal complexes in aqueous media [27,28]. Increasing the % surfactant added to the post-column reagent solution over the range 0–4% resulted in a steady increase in the detector response for Be(II) over the range 0–2%, such that, at the 2% concentration, the peak obtained for 0.1 mg/l Be(II) was increased by a factor of 3. However, above 2% there was no further significant improvement in sensitivity due to an increase in background noise, and thus on the basis of highest signal-to-noise ratio, 2% Triton X-100 was found to be the optimum concentration.

Fig. 3A shows the chromatogram obtained for a 2 mg/l Be(II) standard, obtained using the above optimised conditions. As can be seen, the peak for Be(II) is both sharp and symmetrical (particularly for chelation ion chromatography, where peak shapes can be significantly broader than those obtained using simple ion-exchange chromatography, even after short retention times), reflecting the relatively fast complexation–dissociation kinetics of the IDA functional group under acidic conditions.

3.3. Linearity, reproducibility, detection limits and interferences

Using the optimised conditions the system exhibited excellent linearity over three orders of magnitude. Over the standard concentration ranges 0.01–0.1, 0.1–1.0 and 1.0–10 mg/l ($n=5$) regression coefficients of $R^2=0.998$, 0.999 and 0.999 were obtained, respectively. Linearity was also calculated using standard addition to a number of water matrices such as tap water (0.01–0.05 mg/l, $n=5$, $R^2=0.997$), river water (0.1–1.0 mg/l, $n=5$, $R^2=0.998$) and simulated seawater (see below) (0.02–0.1 mg/l, $n=5$, $R^2=0.996$).

Table 1 shows the system reproducibility and absolute detection limits obtained in various sample matrices. As can be seen from Table 1, reproducibility was investigated with the repeat injection of both high and low standard solutions, with RSDs of less than 1% obtained for retention time, peak height and peak area. Absolute detection limits (250 μl injection volume) were also calculated for Be(II) in various sample matrices, namely, deionised water, tap water, wastewater and simulated seawater. It was found that the ionic strength of the sample matrix caused a slight broadening of the peak shape for Be(II) at concentrations close to the detection limits. However, peak areas were unaffected. Fig. 4 illustrates this effect at the 10 μg/l Be(II) level in (A) deionised water and (B) spiked tap water. The peak areas for the two injections were 37 599 and 37 389, respectively, less than 1% difference.

As mentioned previously, both the selectivity of the stationary phase and post-column reaction detection is suited for the determination of Be(II) in the

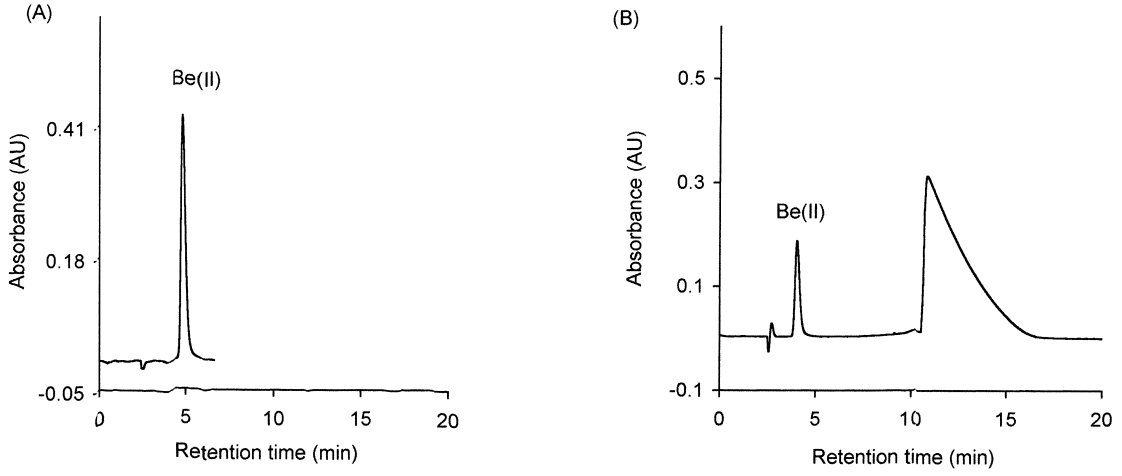


Fig. 3. Chromatograms showing (A) the Be(II) peak for a 2 mg/l standard and (B) the peak for 1 mg/l Be(II) in the presence of 5 mg/l Mn(II), Co(II), Zn(II), Cd(II), Ni(II), Pb(II), Cu(II), Fe(III) and Al(III). Eluent conditions: 0.4 *M* KNO_3, pH 2.5.

Table 1
Reproducibility and detection limits

Concentration Be(II) (mg/l)	Reproducibility RSD (%, $n=8$)		
	Retention time	Peak height	Peak area
2.0	0.55	0.08	0.49
0.05	0.45	0.22	0.85
Sample matrix	Absolute detection limits[a] [ng Be(II)]		
Milli-Q water	0.75 (±0.1 ng)		
Tap water	1.0 (±0.1 ng)		
Waste water	1.0 (±0.1 ng)		
Seawater[b]	2.75 (±0.5 ng)		

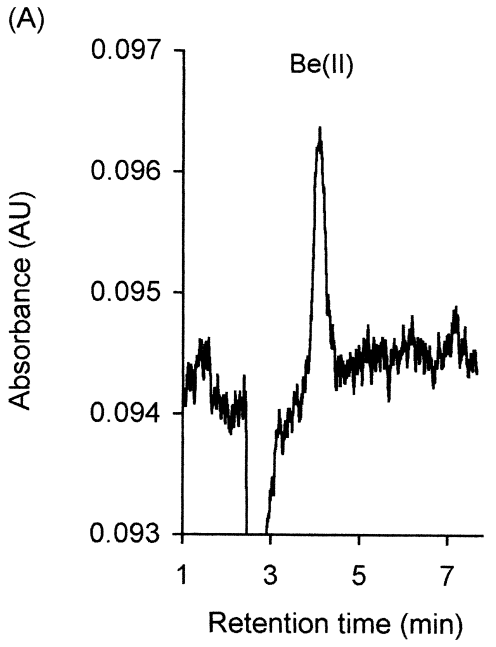
[a] Calculated as twice the peak-to-peak baseline noise, 250 μl injection.
[b] Seawater composition=1300 mg/l Mg(II), 400 mg/l Ca(II) and 0.5 *M* NaCl.

presence of excess concentrations of alkali and alkaline-earth metals. To illustrate this selectivity, a simulated seawater matrix was prepared, consisting of 0.52 *M* NaCl, 1,300 mg/l Mg(II) and 400 mg/l Ca(II). The simulated sample was spiked with trace levels of Be(II) at concentrations of between 0.02 and 2 mg/l. The eluent pH was increased to 3.0 to increase the retention of Be(II) and so resolve the Be(II) peak from a large negative peak at the eluent front resulting from the non-retained matrix ions. In the resultant chromatograms Be(II) was eluted as a reasonably sharp, well resolved peak at a retention time of 5.5 min. Fig. 5 shows the overlaid chromatograms of the simulated seawater itself and the simulated seawater spiked with 0.04 mg/l Be(II). Such a complex sample matrix truly represents a challenge to most analytical techniques with with ratios of Be(II) to Na, Mg(II) and Ca(II) of 1:300 000, 1:32 500 and 1:10 000, respectively.

Selectivity as regards other transition and heavy metal ions was also investigated, as these may also be present at higher concentrations in natural and industrial waste water samples. To investigate these possible interferences, injections of a 1 mg/l Be(II) standard spiked with 5 mg/l of each of the following metal ions were carried out; Mn(II), Co(II), Zn(II), Cd(II), Ni(II), Pb(II), Cu(II), Fe(III) and Al(III). All of the above metal ions, under the eluent conditions developed above, eluted between 10 and 15 min and did not interfere with the determination of Be(II). When a combined standard was prepared containing all of the above metals at 5 mg/l and Be(II) at 1 mg/l, a single large tailed peak resulted, but this was again well resolved from the earlier eluting Be(II) peak. This chromatogram is shown next to the standard Be(II) chromatogram in Fig. 3.

3.4. Analysis of a certified reference wastewater

The developed method was applied to the determination of trace Be(II) in a certified reference freshwater sample NIST 1640. The sample contained excess concentrations of Na, Ca(II) and Mg(II) at concentrations of between 6 and 29 mg/l, as well as Sr(II), Ba(II), Cd(II), Co(II), Pb(II), Cu(II), Ni(II), Zn(II), Al(III) and Fe(III) at concentrations between 20 and 150 μg/l. The sample was itself was analysed using a standard calibration technique and standard addition ($n=4$) to check for possible matrix effects. Analysis of the sample and standards were carried out in triplicate, using a 250-μl injection loop and an eluent pH of 2.5. The two calibration methods resulted in mean values for Be(II) of 35.3 (±0.5) and 34.0 (±0.5) μg/l, respectively, which compared extremely well with the certified value of 34.94±0.41 μg/l. Fig. 6 shows the overlaid chromatograms of the tested reference material and the same sample spiked with 20, 40, 60 μg/l Be(II). Once again the chromatogram illustrates the totally unique selectivity the IDA column exhibits for Be(II), with the peak being well resolved from the other unretained alkaline-earth metals and also the



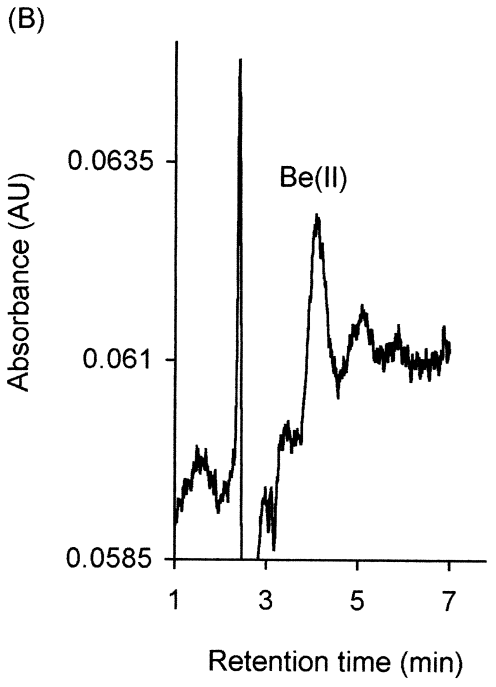


Fig. 4. Chromatograms showing (A) 10 μg/l Be(II) standard in deionised water and (B) 10 μg/l Be(II) spiked into tap water sample. Eluent conditions: 0.4 *M* KNO_3, pH 2.5.

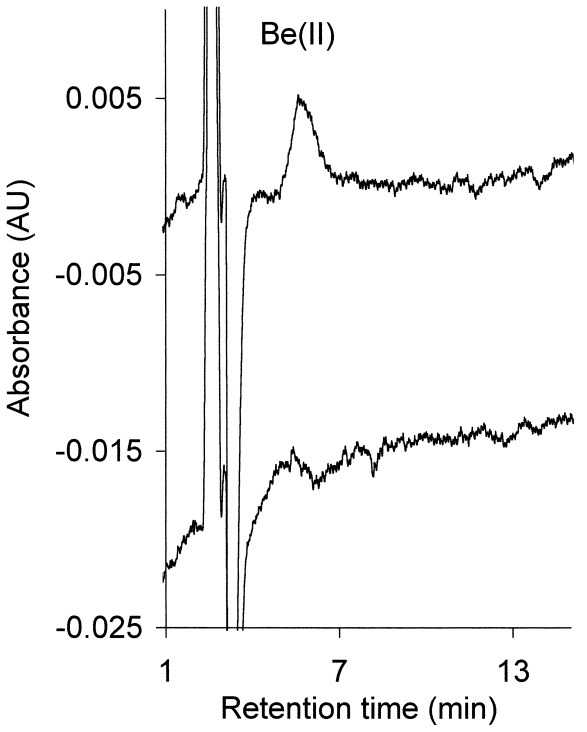


Fig. 5. Overlaid chromatograms of simulated seawater and simulated seawater spiked with 0.04 mg/l Be(II). Eluent conditions: 0.4 *M* KNO_3, pH 3.0.

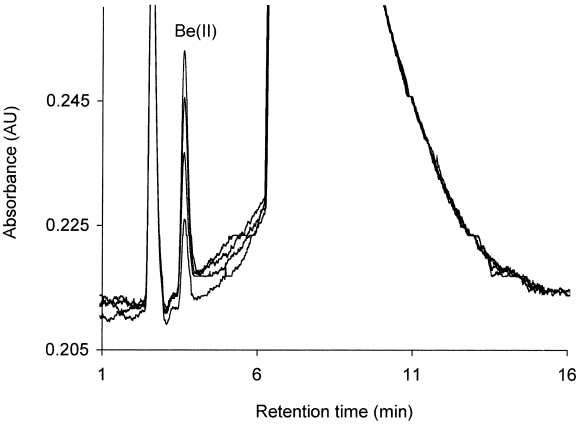


Fig. 6. Overlaid chromatograms of reference material NIST 1640 and the same sample spiked with 20, 40, 60 μg/l Be(II). Eluent conditions: 0.4 *M* KNO_3, pH 2.5.

large combined peak for the common transition and trivalent metal ions.

4. Conclusions

A sensitive and selective chromatographic method for the determination of Be(II) in differing water samples has been developed, that represents a simple alternative to complex atomic spectroscopic methods. The method requires only simple chromatographic instrumentation but is both linear over several orders of magnitude and highly reproducible. The selectivity obtained from the IDA-silica column is such that Be(II) can be detected at low-μg/l concentrations in samples containing excess levels of common matrix metal ions without interference. In addition, the fact that retention is predominantly obtained through stationary phase complexation and not ion-exchange means sample ionic strength has only little effect upon the chromatography of Be(II), allowing samples containing up to 0.5 *M* NaCl to be injected directly.

Acknowledgements

The authors wish to thank the Research Committee of Dublin City University for the provision of a post-graduate studentship to carry out this work.

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