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Iminodiacetic acid functionalised monolithic silica chelating ion exchanger for rapid determination of alkaline earth metal ions in high ionic strength samples

Edel Sugrue,[a] Pavel Nesterenko[b] and Brett Paull*[a]

[a] *National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland. E-mail: Brett.Paull@dcu.ie; Fax: 00353-(1)-7005503; Tel: 353-(1)-7005060*

[b] *Department of Analytical Chemistry, Moscow State University, Moscow, 19899, Russian Federation. E-mail: PavelN@analyt.chem.msu.ru; Fax: 007-(095)-939-46-75; Tel: 007-(095)-939-44-16*

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Iminodiacetic acid has been covalently bonded to a bare silica monolith to produce the first reported high-performance monolithic chelating ion exchange column. Using the new column, separation and determination of traces of alkaline earth metal ions (low ppm) in high ionic strength samples (up to 2 M NaCl and KCl brines), could be achieved in under 40 s. At an eluent flow rate of 4 mL min^{-1} retention time precision was < 1.2% (n = 9) for Mg(II) and Ca(II), with detector linearity (n = 5) over the range 2–10 mg L^{-1} of between R^2 = 0.985 and R^2 = 0.995. In 1 M KCl and NaCl brine samples, detection limits of 0.2 mg L^{-1} were possible.

Silica based monolithic HPLC columns have received much attention in recent years, particularly those modified for reversed-phase separations. The advantages of utilising silica based monoliths for chromatographic separations are well documented, and are predominantly related to the lower back pressures associated with the monolithic column and the excellent peak efficiencies possible at higher than usual flow rates, which allows faster chromatographic separations than previously possible.[1]

For ion exchange separations, silica based monolithic columns have received only limited attention. As yet there are no commercially available ion exchange functionalised monolithic columns designed for high-performance separations of anions or cations. In the case of anion separations this may be due to the common use of basic eluents in anion exchange chromatography, (particularly when used with suppressed conductivity detection) which are incompatible with silica based columns. However, Hatsis and Lucy have recently developed an ion-interaction method utilising a reversed-phase monolithic column for the rapid separation of common inorganic anions. An eluent containing tetrabutylammonium-phthalate as the ion-interaction reagent was used at elevated flow rates, enabling total run times as short as 15 s.[2] More recently, Hatsis and Lucy used the same reversed-phase monolithic column, this time semi-permanently coated with didodecylmethylammonium bromide for the rapid ion exchange separation of inorganic anions combined with suppressed detection, utilising a neutral pH *o*-cyanophenol eluent (pK_a 6.9).[3]

The coating of reversed-phase monolithic columns is also the only approach so far taken for the rapid separation of inorganic cations. Xu *et al.*[4] have recently investigated a monolithic silica reversed-phase column coated with lithium dodecylsulfate for the high speed determination of acidity. The method allowed the separation of hydronium ions from mono- and divalent alkali and alkaline earth metals and was applied to the determination of acidity in rainwater samples. The obvious drawbacks of dynamically modified ion-exchangers are time-consuming reequilibration of the column and problems associated with the use of gradients for improved separations. These can be easily overcome by the use of monolithic columns with chemically attached ion-exchange groups.

The following communication describes early results obtained using a covalently bonded monolithic silica iminodiacetic acid (IDA) chelating ion exchange column. The monolithic chelating ion exchanger was produced through on-column modification with IDA-functionalised silane, resulting in a relatively high capacity column, which exhibited selectivity and efficiency comparable with a standard commercially available 0.4 × 25 cm 8 μm particle size silica gel IDA column. A potential industrial application of this novel high-performance chelating phase is demonstrated with the high throughput analysis of concentrated sodium and potassium brines for alkaline earth metal impurities.

Experimental

Modification of silica monolith

A PEEK lined bare monolithic silica column (Performance SI) of 10 cm length and 4.6 mm id was purchased from Merck KGaA (Damstadt, Germany). According to the manufacturer the silica monolith had a surface area of 300 m^2 g^{-1}, with a 2 μm macroporous and 13 nm mesoporous structure. Before modification the surface of the silica monolith was activated by washing the column placed in a thermostated water bath with distilled water (DW) under 60 °C for 4 h. The modification of the column with IDA groups was performed at 70 °C by recycling 80 ml of a water solution containing a mixture of γ-glycidoxypropyltrimethoxysilane and IDA (both from Fluka Chemie GmBH, Buchs, Switerland) through the column. The recycling system consisted of a glass beaker containing the reagent, a Waters model 510 HPLC pump (Waters, Milford, USA) and the thermostated silica monolithic column. The reagent mixture was recycled at a flow-rate 0.5 mL min^{-1} for 6 h. Then the column was washed with 0.01 M nitric acid for approximately 1 h and equilibrated with the eluent before use.

Reagents

The eluent and post-column reagent (PCR) solutions were prepared using deionised water from a Millipore Milli-Q water purification system (Bedford, MA, USA). The post-column reagent used was 0.4 mM *o*-cresolphthalein complexone (*o*-CPC), 0.25 M boric acid adjusted to pH 10 using NaOH (monitored at 570 nm), purchased from Sigma-Aldrich (Gillingham, Dorset, UK), and used without further purification.

Potassium nitrate, potassium chloride and sodium chloride salts were all obtained from Fluka Chemie (Buchs, Switzerland), as was the nitric acid used for control of eluent pH. All eluents, reagents and standard solutions prepared were filtered through a 0.45 μm filter and degassed using sonication. Low level standard solutions of all metal ions were generally prepared freshly each day from stock solutions (1000 mg L^{-1}) and stored in 1% nitric acid.

Chromatographic conditions

A Dionex Model GPM2 Gradient Pump Module (Sunnyvale, CA, USA) was used to deliver the eluent (1.0–5.0 mL min^{-1}). An automated injection valve, fitted with a 20 μL injection loop was used for the introduction of standards and samples. The particle type silica IDA column (8 μm particle size, 130 Å pore size, 250 × 4.0 mm id) used for comparison with the IDA-monolith was supplied by BioChemMack (Moscow, Russia). A pressure driven Dionex Reagent Delivery Module was used for the introduction of the post column reagent (PCR) (although a Waters model 510 HPLC pump (Waters, Milford, USA) was used to deliver the PCR at eluent flow rates >4 mL min^{-1}), which was then mixed at room temperature with the eluent using a 0.5 m PEEK reaction coil (0.01″ id). A Waters model 486 UV/Vis detector (Waters, Milford, USA) was used at 572 nm to monitor the resultant chromatograms. Data acquisition was at a rate of 10 Hz with processing of chromatograms performed using a PeakNet 6.0 chromatography workstation (Dionex).

Results and discussion

Capacity and selectivity

As mentioned above, unlike silica gel type stationary phases, modification of silica monoliths can only be carried out 'in-column'. Therefore it was important to evaluate the new monolithic IDA column for capacity and selectivity in comparison with a commercially available IDA modified silica gel column. This was carried out to determine whether surface coverage of the silica skeleton was of an order similar to that of silica gel type phases and if the silica structure had any substantial affect upon selectivity for metal ions. The selectivity and mode of retention of IDA functionalised silica gels has been thoroughly investigated in recent years in a number of detailed studies.[5–8] The selectivity of the IDA group for alkaline earth, transition and heavy metal ions is well documented, together with the relatively low affinity for alkali metal ions, meaning IDA columns are particularly suited to the determination of the above groups of metals in high ionic strength samples such as NaCl and KCl brines. In this study we compared the new monolithic column with the IDA silica gel column for their selectivity for alkaline earth metal ions. Of particular interest to us was the performance of the new phase under high ionic strength conditions, where stationary phase complexation would be the dominant retention mechanism.

Fig. 1 shows the chromatograms obtained for the alkaline earth metals, using similar eluents, with the new monolithic IDA column and those obtained using the standard 25 cm silica gel IDA column. The eluents used consisted of (a) 0.3 M KNO_3, adjusted to pH 4.2 for the silica gel column and pH 4.85 for the monolithic column (the difference in pH reflects a lower total column capacity for the monolithic phase (~75 μmol IDA per monolith compared to ~185 μmol IDA on the silica gel column[9]), although given the difference in the lengths of the two columns, the actual surface coverage of the monolithic phase should be very similar), and (b) 0.5 M KNO_3, adjusted to pH 4.2 for the silica gel column and pH 4.85 for the monolithic column. As can be seen from the chromatograms shown, the monolithic IDA column exhibits remarkably similar selectivity and efficiency to the modified silica gel column. The slightly higher retention of Ca(II) on the monolithic phase relative to the other alkaline earth metals is due to the slightly higher eluent pH, which with further increases in eluent pH allowed Ca(II) to be selectively retained, meaning the column could be applied to the determination of Mg(II), Sr(II) and Ba(II) in samples containing excess Ca(II). Taken from the chromatograms shown in Fig. 1, for the Mg(II) and Ca(II) peaks, the average peak efficiencies (N m^{-1}, determined using $N = 5.55t_R^2/w_{½}^2$) were 37,560 and 18,000 for the new monolithic phase, compared to 34,052 and 30,188 for the commercial silica gel column. Eluents ranging from 0.1 to 1 M KNO_3 were investigated with the monolithic column, with resulting selectivity changes being identical to that seen earlier with the silica gel column.[8] These similarities made it clear the retention mechanism for the alkaline earth metal ions on the monolithic IDA column was the same combination of ion-exchange and chelation as seen earlier,[8] meaning application to the rapid analysis of high ionic strength samples was possible.

Rapid separations

The efficiency of the monolithic IDA column was evaluated at elevated flow rates. Previous work by Hatsis and Lucy[3] with

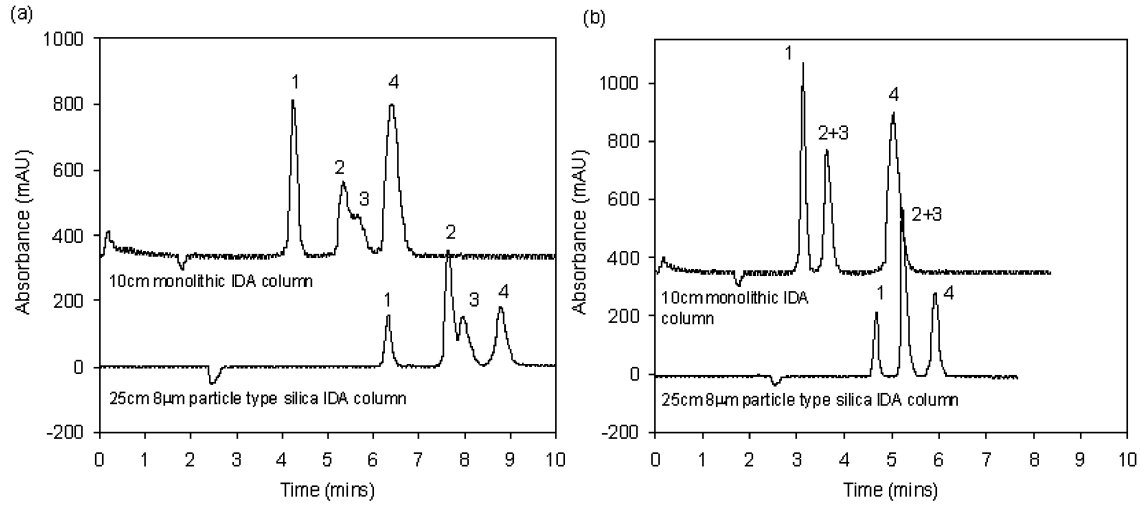

Fig. 1 Chromatograms showing the separation of 1, Mg(II), 2, Sr(II), 3, Ba(II) and 4, Ca(II), using an eluent of (a) 0.3 M KNO_3, adjusted to pH 4.2 for the silica gel column and pH 4.85 for the monolithic column, and (b) 0.5 M KNO_3, adjusted to pH 4.2 for the silica gel column and pH 4.85 for the monolithic column. Flow rate = 1 mL min^{-1}.

coated monoliths for anion separations investigated the effect of flow rate upon peak efficiencies, with flow rates of up to 16 mL min^{-1}. For practical purposes in this study into efficiency the maximum eluent flow rate investigated was 4 mL min^{-1}. This was seen as sufficient to allow sub-1 min run times and did not cause excessive back-pressure (< 120 bar) or significant problems with the mode of detection being applied, namely post-column reaction. Fig. 2 shows the results obtained for 10 mg L^{-1} Mg(II) and Ca(II) standards prepared in either DW or 1 M KCl. As can be seen from the graphs shown it is clear that in both cases some loss of efficiency is seen at the elevated flow rates, but that this effect is much more pronounced for the standards prepared in the 1 M KCl brine solution. As the sample matrix and eluent cations are both K^+ and both present at the same concentration (1 M), this effect must be due to the high matrix Cl^- concentration causing increased band broadening at the higher flow rates. This effect obviously must be considered when analysing high ionic strength samples at higher flow rates, and standard addition calibration used for quantitative analysis. Interestingly, the curves obtained for standards prepared in DW appear to be levelling off at flow rates higher than 4 mL min^{-1}, this being particularly evident with Ca(II). This would indicate that for low ionic strength samples, the column could be used at even higher flow rates (4–10 mL min^{-1}) without further substantial loss in efficiency (provided a suitable detection method could be found).

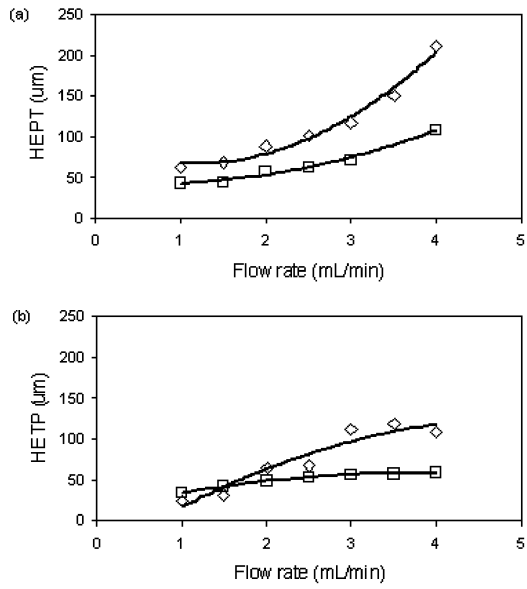

Fig. 2 Effect of eluent flow rate on peak efficiency for (a) 10 mg L^{-1} Mg(II) (◊) and Ca(II) (□) standards prepared in 1 M KCl, and (b) 10 mg L^{-1} Mg(II) (◊) and Ca(II) (□) standards prepared in DW. Eluent = 1 M KNO_3, pH 4.85.

Application to KCl and NaCl brines

The chromatograms in Fig. 3(a) show the separation of 10 mg L^{-1} Mg(II) and Ca(II) in a 1 M KCl brine solution, separated using eluent flow rates of 1.0, 2.0 and 3.5 mL min^{-1}. The chromatograms shown illustrate a reduction in sensitivity at the higher flow rates due to the problem of introducing the PCR into the post-column eluent flow at the higher flow rates using the pressure driven Dionex Reagent Delivery Module. However, the PCR used was highly sensitive and selective for Mg(II) and Ca(II) ions, resulting in a approximate detection limit of 0.2 mg L^{-1} for each ion in the 1 M brine solution. Fig. 3(b) illustrates the potential of the IDA monolithic phase for application to process analysis of brines or high throughput sample screening. The chromatograms compare the 10 cm monolithic column with the 25 cm silica gel column for the separation of Mg(II) and Ca(II) in 1 M KCl brine samples, under eluent flow conditions which result in the same back pressure for the two columns, approximately 110 bar (3.5 mL min^{-1} for the monolithic column and 1.0 mL min^{-1} for the silica gel column).

Fig. 4 shows the separation of Mg(II) and Ca(II) obtained using the new monolithic IDA column when analysing a 2 M KCl sample. In this example a 1 M KCl eluent was used at a flow rate of 5 mL min^{-1}. At this eluent flow rate an additional HPLC pump was required to deliver the PCR, as the above pressure driven Reagent Delivery Module could not provide sufficient flow. The introduction of the second pump did cause some obvious additional 'pump noise', but as can be seen from the chromatogram shown, no system peak due to excess K^+ was evident and the analyte peaks were clearly visible and well

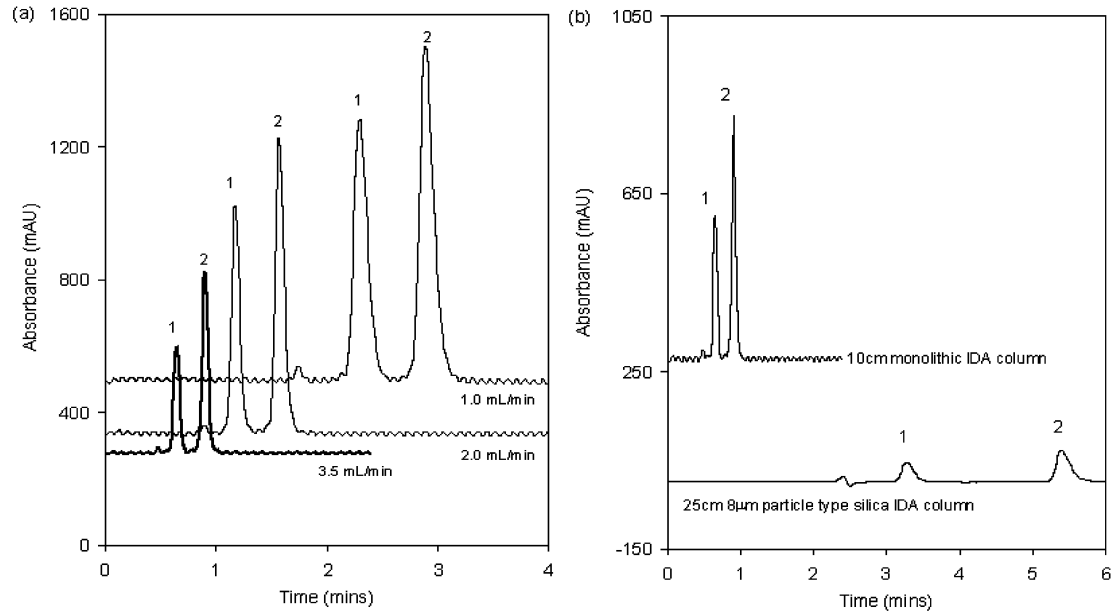

Fig. 3 Chromatograms showing (a) the separation of 1, 10 mg L^{-1} Mg(II) and 2, 10 mg L^{-1} Ca(II) in 1 M KCl solution, using an eluent of 1.0 M KNO_3, adjusted to pH 4.85, at flow rates of 1.0, 2.0 and 3.5 mL min^{-1} using the monolithic column, and (b) the separations of Mg(II) and Ca(II) in 1 M KCl solutions obtained using the 25 cm IDA silica gel column (eluent = 1 M KNO_3, pH 4.90, flow rate = 1.0 mL min^{-1}, analyte conc. = 1.0 mg L^{-1}) and the 10 cm IDA monolithic column (eluent = 1 M KNO_3, pH 4.85, flow rate = 3.5 mL min^{-1}, analyte conc. = 10 mg L^{-1}).

resolved in an analysis time of under 40 s. It is worth noting that in this sample the ratio of matrix ion to analyte ion is approximately 8,000:1 and the sample can be injected directly, without any pre-treatment, with an analysis rate of > 90 samples h^{-1}. This is considerably faster than previously published methods, including those employing spectrophotometry and FIA (which are only single analyte methods).[10–14]

Quantitative performance

The quantitative performance of the described system was evaluated under elevated eluent flow conditions, using a 1 M KNO_3 eluent (pH 4.85). At a flow rate of 4 mL min^{-1}, retention time precision was determined using a 6 mg L^{-1} mixed standard prepared in 1 M KCl. Nine repeat injections resulted in average retention times of 0.574 min for Mg(II) and 0.810 min for Ca(II) with standard deviations of 0.007 min (1.17 %RSD) and 0.007 min (0.81 %RSD) respectively. Linearity was determined over the range 2–10 mg L^{-1} (n = 5) for standards prepared in both 1 M and 2 M KCl. Correlation coefficients of between R^2 = 0.9845 and R^2 = 0.9952 were obtained. The resolution of the Mg(II) and Ca(II) peaks was also calculated for each mixed standard injected and found to range from 2.56 to 2.79 for standards prepared in 1 M KCl, to 2.10 to 2.38 for standards prepared in 2 M KCl. Laboratory grade KCl and NaCl salts (1 M solutions) were analysed using standard addition for Mg(II) and Ca(II) impurities. Standard additions ranging from 0.25 to 10.0 mg L^{-1} Mg(II) and Ca(II) (n = 6) were investigated. Standard addition calibration graphs were again linear for each sample solution, ranging from R^2 = 0.9932 to R^2 = 0.9987, with the concentration of Mg(II) found to be 0.37 mg L^{-1} in the 1 M KCl solution and < 0.2 mg L^{-1} in the 1 M NaCl solution. For Ca(II), concentrations of 0.85 and 0.26 mg L^{-1} were found respectively.

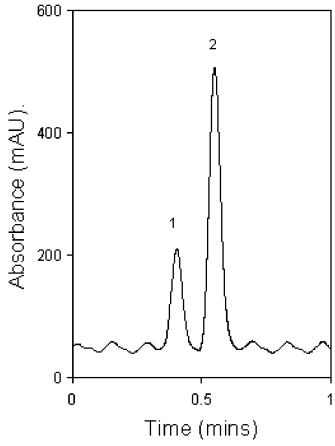

Fig. 4 Chromatogram showing the separation of 10 mg L^{-1} Mg(II) and 10 mg L^{-1} Ca(II) in 2 M KCl (15% w/w) solution in under 40 s. Peaks; 1 = Mg(II), 2 = Ca(II). Eluent = 1 M KCl, pH 4.85, flow rate = 5 mL min^{-1}.

Conclusions

The above communication details early investigations in a novel chelating ion exchange column based upon a monolithic silica rod. This is the first such high-performance chelating ion exchanger produced which can be used for the rapid and efficient separation of cations in high ionic strength matrices. The potential application of this type of column for high throughput screening of such samples is clear and further characterisation and application of this column is currently underway.

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