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The use of a polymer inclusion membrane as a sorbent for online preconcentration in the flow injection determination of thiocyanate impurity in ammonium sulfate fertilizer

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ABSTRACT

A polymer inclusion membrane (PIM) is used for the first time as a sorbent in the construction of a preconcentration column to enhance the sensitivity in flow injection analysis (FIA). The PIM-coated column is readily prepared by coating the PIM containing poly(vinyl chloride), Aliquat 336, and 1-tetradecanol onto glass beads packed in a glass tube. The determination of trace amounts of thiocyanate in ammonium sulfate fertilizer demonstrates the potential of the proposed PIM-coated column in FIA. Thiocyanate standards or samples of relatively large volume (e.g. up to 2000 μL) are injected into a nitrate carrier stream. The sample zone passes through the proposed preconcentration column where thiocyanate is concentrated in a smaller volume of a carrier solution thus resulting in up to 7.4 fold increase in sensitivity. Thiocyanate is detected spectrophotometrically after its reaction with Fe(III) downstream of the preconcentration column. The limits of detection of thiocyanate in the absence and presence of 20 g L^{-1} ammonium sulfate ($S/N=2$) are 0.014 and 0.024 mg L^{-1}, respectively. Thiocyanate was successfully determined in several samples of ammonium sulfate fertilizer.

1. Introduction

Even though flow injection analysis (FIA) with spectrophotometric detection is a simple, rapid, and highly reproducible technique, its sensitivity is sometimes insufficient to determine a target species in real samples without preconcentration, and online solid-phase extraction, using ion-exchange or chelating resin, can be conveniently utilized for this purpose [1].

In recent years, polymer inclusion membranes (PIMs) have attracted a great deal of attention in various fields including analytical science because of their potential as solid-phase extraction materials [2–6]. A PIM generally consists of a base polymer, such as poly(vinyl chloride) (PVC) and cellulose triacetate (CTA), an extractant, and a plasticizer or modifier. In solid-phase extraction using a PIM containing an appropriate extractant, the extraction and back-extraction of a target chemical species (e.g. small inorganic or organic molecules or ions [2–6]) can be achieved on the basis of almost the same mechanism as for the corresponding liquid–liquid extraction systems [2,3]. A PIM can also be applied to the transport of a target chemical species [2–6] where the PIM is placed between the donor and acceptor solutions, and the target chemical species is extracted from the donor solution and back-extracted into the acceptor solution. It is noteworthy that the characteristics of a PIM are easily tunable to the extraction/back-extraction of the target chemical species by changing the components of the PIM. Also, the cost of preparing a PIM is much lower than that of an ion-exchange or chelating resin [7,8]. In many cases, a PIM having a flat sheet form is used because it is readily prepared by a casting technique [2–6,9–13]. Solid-phase extraction using PIMs has been applied to the determination of zinc(II) [9,10] and orthophosphate [11] using FIA, glyphosate and aminomethylphosphonic acid using capillary electrophoresis [12], and oxytetracycline using high performance liquid chromatography [13]. In these cases, the PIM was used as a semi-permeable medium for the transport of the target chemical species. On the other hand, PIMs can be readily coated onto various supports. A hollow fiber PIM has been prepared by employing a commercially available CTA hollow fiber swelled in chloroform containing extractant and plasticizer [14] and was used for the transport of cerium(III). We considered that it should also be possible to prepare a packed column coated with a PIM as a sorbent, which can be used for online preconcentration in FIA. To the best of our knowledge, the application of PIM-coated columns in FIA has not been previously reported.

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In this study, a FIA system utilizing online solid-phase extraction in a PIM-coated column is investigated in detail. As proof of concept, the thiocyanate ion was chosen as the target analyte with a PIM composition consisting of PVC as the base polymer, Aliquat 336 as the extractant and 1-tetradecanol as a modifier. This PIM has been shown to effectively extract thiocyanate which can be readily back-extracted with a sodium nitrate solution [15]. For the preparation of the column, the PIM has been coated onto glass beads packed in a glass tube.

It is known that thiocyanate causes growth inhibition of plants [16]. Ammonium sulfate, which is widely used as a chemical fertilizer, can contain some thiocyanate as an impurity because in many cases by-product ammonium sulfate from the coking industry is utilized for producing the fertilizer [17]. The concentration of thiocyante in ammonium sulfate fertilizer can be determined by ion chromatography (IC) as proposed by Incorporated Administrative Agency—Food and Agricultural Materials Inspection Center (Japan) [18].

The present paper describes a simpler and less expensive in terms of instrumentation and reagents FIA method for the determination of traces of thiocyanate in ammonium sulfate fertilizer which illustrates the potential of PIM-coated columns for online preconcentration in flow analysis.

2. Experimental

2.1. Apparatus

A Gilson Minipuls 3MP-2 peristaltic pump (France) was used in the preparation of PIM-coated columns. The FIA system was assembled using a Minipuls 3MP-2 peristaltic pump, an EYELA SV-6005N sample injector (Japan), and a Jasco UV-970 UV/vis detector equipped with a Jasco PTFE flow cell (Japan) (Fig. 1). PTFE tube (0.5 mm of inner diameter) was also used in this system.

A Hitachi U-1800 spectrophotometer (Japan) was used in the determination of thiocyanate during the evaluation of the PIM-coated column for solid-phase extraction of thiocyanate.

2.2. Reagents

Deionized water (Elix-UV3, Merck Millipore, USA) was used in all experiments. PVC (Selectophore, Fluka, USA), Aliquat 336 (Aldrich, USA), 1-tetradecanol (Aldrich) [15], and tetrahydrofuran (THF, dehydrated, stabilizer free, Kanto Chemical, Japan) were used for preparing PIM-coated columns. A standard solution of thiocyanate (1000 mg L^{-1}) was prepared by dissolving potassium thiocyanate (guaranteed reagent grade, Kanto Chemical, Japan) in deionized water [19]. The solution was diluted to the appropriate concentration with deionized water before use. The other reagents used in this study were of analytical or guaranteed reagent grades.

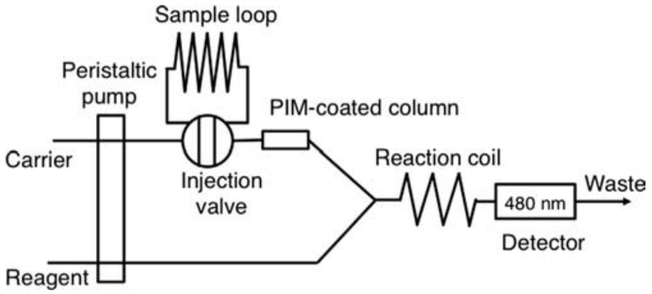

Fig. 1. Schematic diagram of the FIA system with the PIM-coated column. Carrier, 1.0 or 0.5 mol L^{-1} $NaNO_3$. Reagent, 0.1 mol L^{-1} $Fe(NO_3)_3$ in 0.1 mol L^{-1} HNO_3.

2.3. Experimental procedures

2.3.1. Preparation of the PIM-coated column

PVC, Aliquat 336, and 1-tetradecanol (total amount, 0.40 g) were dissolved in 7.5 mL of THF. Glass beads (diameter, 0.35–0.50 mm, As One, Japan) were packed into a glass tube (length, 50–200 mm, inner diameter, 2 mm), and the glass tube was capped with a small amount of silica wool. A THF solution of the PIM components was drawn into the packed with glass beads glass tube using a peristaltic pump, and the solution was then discharged from the column by aspirating air through the column using the same peristaltic pump. This operation was repeated three times. After that, air was continuously passed through the glass tube for 40 h at a flow rate of approximately 100 mL min^{-1} to remove the THF from PIM coating of the column.

2.3.2. Studying the suitability of the proposed PIM-coated column for preconcentration of thiocyanate

A solution (10 mL) containing 5.0 mg L^{-1} of thiocyanate was passed through the PIM-coated column using the peristaltic pump at a flow rate of 0.1 mL min^{-1}. The back-extraction of the thiocyanate was conducted by passing 10 mL of 1.0 or 0.5 mol L^{-1} sodium nitrate solution at the same flow rate. The thiocyanate concentration in the solution leaving the column was determined by spectrophotometry at 480 nm using 0.1 mol L^{-1} of iron(III) nitrate solution containing 0.1 mol L^{-1} nitric acid.

2.3.3. Determination of thiocyanate using the proposed FIA system with the PIM-coated column

A sample solution (100–2000 μL) was injected into a carrier stream containing sodium nitrate. The solution was passed through the column and thiocyanate was extracted into the PIM coating of the glass beads and internal walls of the glass tube. This was followed immediately by back-extraction of thiocyanate with the sodium nitrate carrier solution. The carrier stream was merged at a confluence point downstream of the column with a reagent stream containing 0.1 mol L^{-1} iron(III) nitrate and 0.1 mol L^{-1} nitric acid and the absorbance of the iron(III)-thiocyanate complex was measured at 480 nm.

The different batches of ammonium sulfate fertilizer used in this study were made in Japan (Sample nos. 1–4) or China (Sample no. 5). Each fertilizer sample (1.0 g) was dissolved in 50 mL of deionized water. The solution was then filtered through a membrane filter (Merck Millipore, Omnipore membrane, 0.2 μm pore size) and the thiocyanate in the filtrate was determined using the FIA procedure outlined above.

3. Results and discussion

3.1. Optimization of the conditions for the preparation of the PIM-coated column

The conditions for preparing the PIM-coated column were optimized using a 200 mm long glass tube with an inner diameter of 2 mm packed with around 0.82–0.93 g of glass beads. A PIM containing 60%(w/w) PVC, 30%(w/w) Aliquat 336, and 10%(w/w) 1-tetradecanol [15] was coated on the inner walls of the glass tube and on the surface of the glass beads as described in Section 2.3.1. The mass of the PIM coating was measured to assess its degree of curing and solid-phase extraction of thiocyanate was conducted to evaluate the extraction potential of the prepared column.

After the THF solution containing PVC, Aliquat 336, and 1-tetradecanol had been drawn into the glass tube packed with glass beads, and excess solution had been removed by aspirating air, the column was then left to dry at room temperature for the removal of the remaining THF. The drying conditions were examined and it was found that a constant mass of the column was obtained after approximately 3 days of drying. The drying time was decreased to 40 h by flowing air through the column at a volumetric flow rate of approximately 100 mL min^{-1}. The mass of the column dried with the use of airflow was smaller than without the use of airflow thus suggesting that some THF was trapped between the glass beads in the latter case. The extracted amount of thiocyanate was larger in columns dried with the help of airflow. In the case of columns prepared without airflow, it was sometimes difficult to pass the carrier solution through the column. This was most likely due to the PIM filling the voids between the glass beads packed in the glass tube. This problem was also observed when the PIM coating solution was discarded from the column using air at a very low flow rate (e.g. 0.1 mL min^{-1} compared to 1.0 mL min^{-1}). In this study, therefore, the excess THF solution in the column was discarded by air at a flow rate of 1.0 mL min^{-1} and the column was then dried by passing air for 40 h at a flow rate of 100 mL min^{-1}. The mass of the column increased when the coating process, including the aspiration and discharge of the THF solution, was repeated several times, however, the mass remained constant after the third repeat. Therefore, conducting the coating process three times was considered to produce optimum PIM coating. This column coating procedure was found to be reproducible when applied to the manufacturing of 18 columns which resulted in an average amount of PIM retained in the columns of 4.4 mg with a standard deviation of 0.6 mg.

The experiments involving the consecutive pumping through the column of 10 mL of a solution containing 5.0 mg L^{-1} thiocyanate and then of 10 mL of a solution containing either 0.5 mol L^{-1} or 1.0 mol L^{-1} sodium nitrate showed that the amount of extracted thiocyanate (37 μg, 19% of the theoretically calculated maximum ion-exchange capacity of the column) was practically quantitatively back-extracted by both sodium nitrate solutions, i.e. 96% or 98%, respectively. These results demonstrate that the PIM-coated column is suitable for online preconcentration of thiocyanate.

3.2. *Application of the PIM-coated column for online preconcetration of thiocyanate in the FIA system*

In FIA, the ability to preconcentrate a target analyte from a large volume of a sample solution into a much smaller volume of solution is advantageous in order to improve sensitivity and possibly selectivity of the analytical determination. When a large volume, for example 2000 μL, of a sample solution containing 1.0 mg L^{-1} of thiocyanate was injected in the FIA system (Fig. 1) without the column, a diffuse and broad peak was obtained as shown in Fig. 2(a). After incorporating the PIM-coated column in the FIA system, well-defined sharp peaks were obtained (Fig. 2(b)–(f)). A pictorial view of the preconcentration process using the PIM-based column is shown in Fig. 3. Initially, the Aliquat 336 in the PIM is present in the chloride form but is rapidly converted to the nitrate form on contact with the carrier. When a large volume of the solution containing thiocyanate is injected into the carrier stream, thiocyanate is retained in the column by ion-exchange with nitrate. As further nitrate carrier flows through the column, the retained thiocyanate is back-extracted and emerges from the column in a small volume of carrier solution. The system parameters, including the column length, the Aliquat 336 concentration in the PIM, the operating conditions of the FIA system, including the injection volume, the concentration of nitrate in the carrier solution, and its flow rate were optimized as described in the following sections.

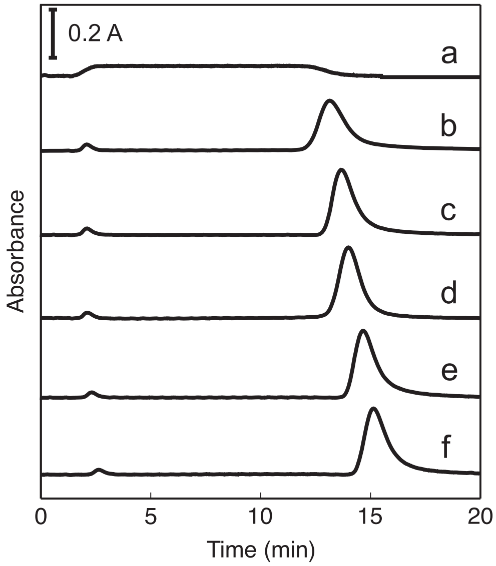

Fig. 2. Peak profiles obtained using the FIA system without the column (a) and with different length columns 5 cm (b)–(d), 10 cm (e), and 15 cm (f). PIM coatings contained 30%(w/w) (b), 40%(w/w) (c), and 50%(w/w) (d)–(f) Aliquat 336 and 10%(w/w) 1-tetradecanol. SCN$^-$ concentration 1.0 mg L^{-1}; injection volume, 2000 μL; carrier, 0.5 mol L^{-1} NaNO$_3$; flow rate, 0.2 mL min^{-1}.

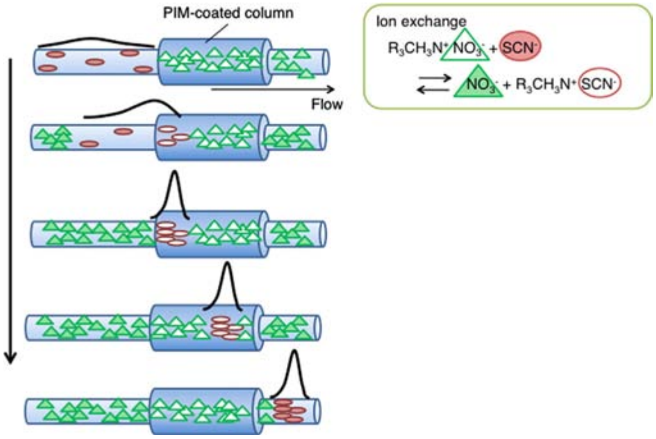

Fig. 3. Schematic diagrams of the proposed mechanism for the concentration of thiocyanate in the PIM-coated column in the FIA system. (●, ▲) SCN$^-$ and NO$_3^-$ in the solution, respectively. (○, △) SCN$^-$ and NO$_3^-$ in the PIM coating, respectively.

3.2.1. *Column conditions*

The influence of the length of the column (i.e. 5, 10, 15, and 20 cm) coated with PIM containing 30%(w/w) Aliquat 336, 10%(w/w) 1-tetradecanol and 60%(w/w) PVC was studied in the FIA system by injecting 2000 μL of 1.0 mg L^{-1} thiocyanate standards. It was found that the peak height increased with the increase in the column length, and became almost constant above 10 cm. The 20 cm column was difficult to prepare in a reproducible fashion because of its length and columns longer than 15 cm were not used in the subsequent experiments. The effect of the Aliquat 336 concentration of the PIM was investigated using the 5, 10, and 15 cm columns. For the different PIM compositions, the amount of 1-tetradecanol was held constant at 10%(w/w) and the concentration of PVC was altered accordingly. As shown in Table 1, the peak height increased with increase in the Aliquat 336 concentration for each column length, but for the PIM containing 50%(w/w) of Aliquat 336 there was a small decrease in the peak height with increase in column length. Visual examination of the peak profiles shows that, without the column, a diffuse and broad peak starts to appear immediately after the injection of the thiocyanate standard

Table 1
Relative peak heights for 5 to 20 cm column lengths and different concentrations of Aliquat 336 in the PIM composition.

Aliquat 336 concentration (%(w/w))	Relative peak height[a]			
	5 cm	10 cm	15 cm	20 cm
30	0.831	1.00	0.992	1.00
40	1.09	1.16	1.09	–
50	1.26	1.18	1.13	–

[a] The relative peak height was calculated based on the peak height for the 10 cm column and 30%(w/w) Aliquat 336.

(Fig. 2(a)). When the 5 cm column coated with the 30%(w/w) Aliquat 336 PIM was introduced into the FIA system, a sharp peak was obtained (Fig. 2(b)) showing that thiocyanate was retained by the column, however, there was some broadening of the peak. This was due to insufficient ion-exchange capacity of the column which led to a lower degree of retention of thiocyanate. Higher thiocyanate retention resulting in higher peaks was obtained with an increase in the concentration of Aliquat 336 in the PIM (Figs. 2 (c) and (d)). The use of longer columns (10 cm and 15 cm) with a 50%(w/w) Aliquat 336 PIM increased the degree of retention even further, however, the peaks showed some tailing, resulting in a decrease in the peak height (Figs. 2(e) and (f)). This was due to the more efficient thiocyanate extraction ability of the PIM-coated columns thus leading to greater retention of thiocyanate. The highest and most symmetrical peaks were obtained for the 5 cm column coated with the 50%(w/w) Aliquat 336 PIM (Fig. 2(d) and Table 1). Since this column was also relatively easy to prepare and use, it was applied in the subsequent investigations.

3.2.2. Operating conditions of the FIA system with a PIM-coated column

For the operation of the FIA system with the PIM-coated column, it was found that a sample injection volume greater than 200 μL was required in order to obtain a detectable peak using a solution containing 1.0 mg L^{-1} of thiocyanate. The effect of the sample volume on the peak height for 1.0 mg L^{-1} thiocyanate standards was investigated in the range of 200–2000 μL. As expected, the peak height increased with increasing the sample volume. It was found difficult to use sample volumes higher than 2000 μL because of the associated high back pressure. Thus, in the subsequent experiments a sample volume of 2000 μL was selected.

The concentration of sodium nitrate in the carrier solution was varied and constant peak heights were obtained for concentrations between 0.5 mol L^{-1} and 2.0 mol L^{-1}. This was the concentration range required for the quantitative back-extraction of thiocyanate to produce sharp peaks with a minimal tailing. The peak height decreased slightly at 2.0 mol L^{-1} because of increased tailing which was also accompanied by a noisy base-line. Thus, 1.0 mol L^{-1} of sodium nitrate solution was determined as the optimum carrier concentration.

In the operation of the FIA system, the flow rates of the carrier and reagent streams were maintained the same. The effect of the flow rate on sensitivity and residence time, which is defined as the time corresponding to peak height, was also investigated. An increase in the flow rate caused some peak tailing resulting in a decrease in peak height. On the other hand, as expected, the residence time increased with decreasing the flow rate. In this study, a flow rate of 0.2 mL min^{-1} was selected as the optimum flow rate to achieve maximum sensitivity.

A linear calibration curve (R^2=0.999) was obtained in the concentration range from 0.02 to 1.0 mg L^{-1} thiocyanate using the optimum conditions of the FIA system. Its slope was 7.4 ± 0.3 (mean ± standard deviation, n=3) times greater than the slope of the calibration curve obtained without the column and this value represents the preconcentration factor associated with the column. The limit of detection (signal to noise ratio=2) was 0.014 mg L^{-1} with the column and 0.110 mg L^{-1} without the column.

3.3. Determination of thiocyanate in ammonium sulfate fertilizer

Validation of the proposed FIA method using the PIM-coated column was performed by applying it to the determination of thiocyanate in ammonium sulfate fertilizer. However, before this, it was necessary to examine if high concentrations of ammonium sulfate would affect the thiocyanate determination.

3.3.1. Effect of ammonium sulfate

The effect of ammonium sulfate was investigated using solutions containing 1.0 mg L^{-1} thiocyanate with concentrations of ammonium sulfate in the range of 0–50 g L^{-1}. As shown in Fig. 4, the peak height for thiocyanate decreased with the increase in the concentration of ammonium sulfate. This effect was observed because the high concentration of sulfate interfered with the extraction of thiocyanate causing peak broadening. Additionally, the base-line also became noisy in the presence of high concentrations of ammonium sulfate. On the other hand, the concentration of thiocyanate as an impurity is expected to increase with increase in the concentration of ammonium sulfate fertilizer. It was concluded that 20 g L^{-1} of ammonium sulfate fertilizer provided good sensitivity with acceptable base-line stability. Thus, the thiocyanate calibration curve was prepared using solutions containing 20 g L^{-1} of ammonium sulfate. It was found to be linear in the concentration range of 0.040 to 1.5 mg L^{-1} thiocyanate (R^2=0.999) with a limit of detection (signal to noise ratio=2) of 0.024 mg L^{-1}. It was necessary to test the effect of small amounts of chloride and nitrate which may be present in the fertilizer and it was found that the tolerance limits for chloride and nitrate, defined as the maximum concentrations which gave more than 90% recovery of thiocyanate, were 3.5 and 0.4 g L^{-1}, respectively.

3.3.2. Determination of thiocyanate in ammonium sulfate fertilizer

The determination of thiocyanate in five samples of commercially available ammonium sulfate fertilizer was carried out and the results are summarized in Table 2. Thiocyanate impurities were detected in only two of the fertilizer samples. However, recovery tests were carried out on all the samples by spiking the

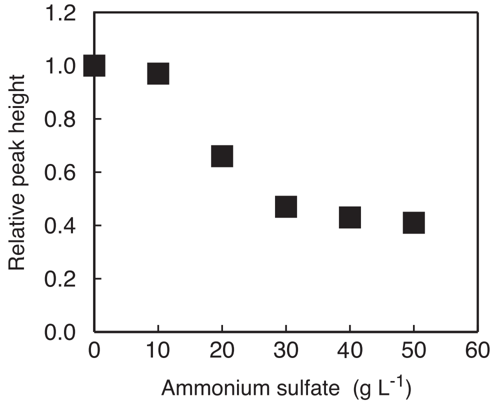

Fig. 4. Effect of the concentration of ammonium sulfate on the thiocyanate peak height. SCN^{-}, 1.0 mg L^{-1}; injection volume, 2000 μL; carrier, 1.0 mol L^{-1} $NaNO_3$.

Table 2
Results for determination of the thiocyanate concentration in ammonium sulfate fertilizer[a].

Sample	Added (mg L^{-1})	Found[b] (mg L^{-1})	Concentration (μg g^{-1})	Recovery (%)
1	–	0.094 ± 0.004	4.7	–
	0.050	0.14 ± 0.00$_7$	–	90
2	–	(0.037 ± 0.003)[c]	(1.8)	–
	0.050	0.088 ± 0.002	–	102
3	–	N.D.	–	–
	0.050	0.053 ± 0.003	–	106
4	–	N.D.	–	–
	0.050	0.050 ± 0.001	–	100
5	–	N.D.	–	–
	0.050	0.050 ± 0.002	–	100

N.D.: Not detected.

[a] Ammonium sulfate fertilizer concentration, 20 g L^{-1}.

[b] Mean ± standard deviation (n=5).

[c] This value was calculated by extrapolating the calibration curve because the concentration was lower than 0.040 mg L^{-1} which was the lowest concentration in the calibration curve.

sample solutions with 0.050 mg L^{-1} thiocyanate. Close to 100% recovery was obtained for all samples. These results validate the suitability of the proposed FIA method using the PIM-coated column for the determination of thiocyanate in ammonium sulfate fertilizer. The results also confirm that an Aliquat 336 PIM-coated preconcentration column is a useful tool in the determination of low concentrations of thiocyanate.

3.4. *Column stability*

The stability of the proposed column was tested over a 6 day period during which 160 thiocyanate calibration standards containing 20 g L^{-1} ammonium sulfate and 20 g L^{-1} ammonium sulfate fertilizer samples were injected. The peak heights of the 0.10 mg L^{-1} thiocyante standard obtained in each of these 6 days were compared. It was found that for the first 3 days and 96 injections there was no change in the peak height after which it gradually decreased to 95% of its initial value after 124 injections (Day 4) and after 159 injections (Day 6) the peak height was 77% of its initial value. These results indicate that the proposed preconcentration column can be used reliably for at least 100 injections.

4. Conclusions

One of the main aims of this research was to expand the application of PIMs in separation science. The results presented in this paper demonstrate for the first time that PIM coated preconcentration columns can be incorporated successfully into FIA systems to improve substantially sensitivity. The PIM-coated columns can be readily prepared by coating the selected PIMs onto glass beads-packed in small diameter glass tubes. In the system reported, a PIM containing Aliquat 336 as carrier has been used to preconcentrate thiocyanate into a small segment of a carrier solution resulting in a large increase of the corresponding FIA peak height. The potential of PIM coated preconcentartion columns in FIA was illustrated with the determination of traces of thiocyanate as an impurity in ammonium sulfate fertilizer. Since the extraction ability of the PIM in the column is readily tunable by varying the PIM composition, the proposed PIM-coated columns are expected to be applicable to the determination of a large range of analytes by FIA.

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