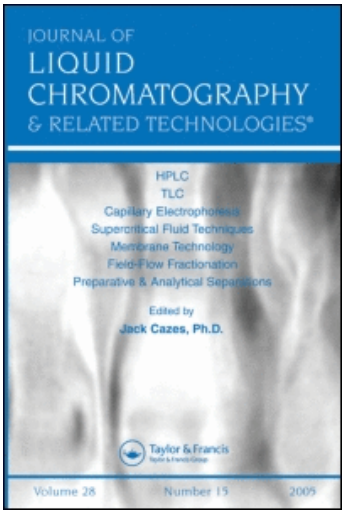

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REDOX CHROMATOGRAPHY USING POLYPYRROLE AS A STATIONARY PHASE

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ABSTRACT

Chromatographic studies on the effect of exposure of polypyrrole coated stationary phases to redox reagents have been carried out. Polypyrrole containing chloride or dodecylsulfate as counterion was chemically synthesized and coated onto silica particles and packed into a chromatographic column. A series of standard compounds was used as the molecular probes. Changes in the chromatographic properties of polypyrrole as the result of the exposure to redox reagents were compared with those obtained by electrochemical treatment.

INTRODUCTION

Polypyrrole (Figure 1) is capable of a diverse array of molecular interactions.[1,2] Polymers with a great variety of properties can be produced by resorting to derivatives,[3,4] copolymers,[5,6] or incorporation of particular anions ($-A^-$)[7,8] during synthesis.

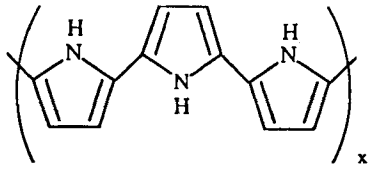


Figure 1. Polypyrrole.

Perhaps the most interesting property of conductive polymers is that their physicochemical properties can be modified *in-situ* by switching the oxidation state, either electrochemically or chemically. Several workers have made use of this property to design special liquid chromatographic columns,[9-11] with conductive packing materials. It has been demonstrated that the retention of analytes can be controlled by application of an electrical potential to the stationary phase.

The properties of conductive polymers can also be modified by exposure to chemical oxidants/reductants.[12-14] To date, however, the effect of chemical oxidation/reduction of conductive polymers on the chromatographic properties and, hence, molecular interaction capabilities, has not been reported. In this work, the effect of exposure to redox reagent solutions has been considered. Two polypyrrole-based conductive polymers, i.e., polypyrrole chloride and polypyrrole dodecylsulfate, were investigated. The redox reagents employed were ferric chloride and sodium sulfite.

For the purpose of the study, the polymers were chemically polymerised directly on the surface of silica particles which were then packed into chromatographic columns. A series of small molecules, polyaromatic hydrocarbons, basic drugs, and amino acids were used as the test compounds. The columns were chemically treated by injecting either ferric chloride or sodium sulfite solution.

EXPERIMENTAL

Reagents and Materials

All reagents were of analytical reagent (AR) grade unless otherwise stated. Pyrrole, LR grade (Fluka Chemika-BioChemika, Buchs, Switzerland) was distilled before use. HPLC grade methanol and acetonitrile were obtained from

Mallinckrodt Australia, Clayton, Victoria, Australia, while the water was purified using a Milli-Q water system from Millipore (Lane Cove, NSW, Australia). Benzene and toluene were purchased from Ajax (Auburn, NSW, Australia). Aniline and theophylline were commercially supplied by BDH (Poole, UK), while N,N-dimethylaniline (DMA) was from May and Baker (Dagenham, UK). Sodium sulfite, ferric chloride, sodium acetate (NaAc), and sodium chloride were from BDH, while sodium dodecylsulfate (SDS) and Tris-(hydroxymethyl amino methane) (Tris) was purchased from Sigma Chemical Co. (Castle Hill, NSW, Australia). Hydrochloric acid and glacial acetic acid (HAc) were obtained from Ajax. L-Tryptophan (Trp) and L-Tyrosine (Tyr) were also obtained from Sigma .

The acetate buffer solution, pH 3.8, was prepared from a mixture consisting of 440 mL 0.2 M HAc, 60 mL 0.2 M NaAc and 500 mL water. The buffer solution, pH 7.4, was prepared by mixing 420 mL 0.1 M HCl with 500 mL 0.1M Tris and 80 mL water. Packing materials were prepared as described previously.[9,10] Silica (Ultrasphere, Beckman Instruments, Gladesville, NSW, Australia) was used as received. The silica has particle size = 10 μm; surface area = 220 m^2/g; and pore size = 80 Å. Stainless steel columns (4.9 mm x 50 mm) were purchased from Alltech (North Strathfield, NSW, Australia). These columns were then packed with either polypyrrole chloride or polypyrrole dodecylsulfate-coated silica, using a column slurry packer, with methanol as the driving liquid. The test samples were dissolved in pure methanol or acetonitrile and diluted with the mobile phases if required. Trp and Tyr were dissolved in water, either individually or as a mixture.

Instrumentation

All chromatographic work was performed with an HPLC system which consisted of a Kortec K35D HPLC pump (ICI, Melbourne, Australia), a Rheodyne 7125 injector with 20 μL sample loop (Alltech), a variable wavelength UV-Vis detector (ICI) and a Kipp and Zonen BD41 strip chart recorder.

An electrochemical cell system, consisting of Pt disc (as working electrode), Ag/AgCl (as reference electrode), and a piece of RVC (as counter electrode) that was connected to a galvanostat (home-made), was used to prepare polypyrrole chloride-coated Pt electrode. A pH meter, Orion SA 520 (Linbrook, Thornleigh, MSW, Australia), was used for electrode potential measurement. Electrochemical redox manipulation was accomplished with a home-made potentiostat.

Chromatographic Measurements

Columns were flushed with water and methanol before use. The mobile phase flow rate was adjusted to 1 mL/min throughout the experiment. The eluent output was monitored at 254 nm. Retention times were recorded with a stopwatch and the dead time (t_0) was estimated from the retention of water. The mobile phase system used was a mixture of water-methanol or water-acetonitrile, the composition of which could be varied as required. The elution of amino acids was carried out with either buffer-methanol or buffer-acetonitrile eluent, depending on which column was being used.

The chromatographic properties of the column were manipulated by treating it with either 0.1 M Na_2SO_3 or 0.1 M $FeCl_3$. The reductant or the oxidant solution was injected into the column through the injector several times, while water was passing through the column at 0.3 mL/min. After each run of several injections, the column was flushed with 50-100 column volumes of water before the mobile phase to be used was employed.

Ferric chloride (E°= +0.771V) was chosen here as the oxidant for the following reasons. Firstly, it was used in the preparation of the stationary phase, thus avoiding any complication which could be brought in if using other chemicals. For example, if $Fe(NO_3)_3$ is used as the oxidant, NO_3^- would be incorporated into the polymer instead of Cl^- and this could change the properties of the film. Secondly, it has been reported that neutral polypyrrole films can be oxidised chemically by various metals such as Fe^{3+}.[15] The resulting oxidised films became more conductive.[16] Sodium sulfite is a common reductant (E^O = -0.93) and, because its reaction products are soluble in water, they are easily removed from the column.

RESULTS AND DISCUSSION

For the preliminary studies, the redox reagents were not included in the eluent, as this would complicate the interpretation of results. The inclusion of the oxidant/reductant in the eluent may also influence the chemical nature of the molecular probes being used and would certainly affect ion exchange processes occurring on the conducting polymer.

Conductive polymer films, such as polypyrrole, can be switched from conducting to non-conducting by reducing the polymer films, and they can be made conductive again by reoxidizing the film. The counterions are expelled during reduction and incorporated during oxidation according to:

$$(PPy)^{+}_{n}\,A^{-}_{(p)} \underset{-e}{\overset{+e}{\rightleftharpoons}} (PPy)^{o}_{n} + A^{-}_{(s)}$$

where $A^{-}_{(p)}$ is the counterion in the polymer and $A^{-}_{(s)}$ is the counterion in solution. This mechanism is applicable especially for small hydrophilic counterions. For large counterions, such as dodecylsulfate (DS^{-}), the situation could be different. According to Panero et al.[17] and Martinez et al.,[18] DS^{-} counterions are not easily released after the incorporation of the ions into the polymer matrix. This is not just because of their large size, but also because of the presence of the polar end and the long alkyl chain in the molecules, the former being compatible with the charged form of the polymer and the latter with the neutral polymer backbone. The counterion movement in the polymer containing such large counterions can be illustrated according to:

$$(PPy)^{+}_{n}\,A^{-}_{(p)} + C^{+}_{(s)} \underset{-e}{\overset{+e}{\rightleftharpoons}} (PPy)^{o}_{n}\,A^{-}_{(p)}\,C^{+}_{(p)}$$

where $C^{+}_{(s)}$ is the counter-cation in solution and $C^{+}_{(p)}$ is the counter-cation in the polymer. During polymer reduction, because the counter-anions are not easy to expel, the counter-cations are incorporated into the polymer to preserve the charge neutrality.

There have been some reports, however, that such large incorporated amphiphilic surfactant anions are released on the reduction of the polymer.[19-22] The loss could be up to approximately 50%.

In the study described hereafter $FeCl_3$ and Na_2SO_3 were used as redox reagents to manipulate the oxidation state of the stationary phases prepared from polypyrrole doped with Cl^{-} and DS^{-}. In oxidation-reduction reactions, the reagents work normally through electron transfer processes according to:

$$Fe^{3+} + e \rightleftharpoons Fe^{2+}$$

$$SO_4^{2-} + H_2O + 2e \rightleftharpoons SO_3^{2-} + 2OH^{-}$$

In the following discussion, a chromatographic examination of the effect of exposure of polypyrrole to the redox reagents is described.

Table 1

Elemental Composition of the Column Packings

Packings	Weight Percent				Mole Ratio		
	C	H	N	Cl	S	N/Cl	N/S
PPCl/Si	4.20	0.31	1.12	1.4	---	2.10	---
PPDS/Si	7.31	0.83	1.17	0.71	0.67	4.17	4.00

Table 2

Effect of Redox Treatment of PPCl/Si and PPDS/Si on Retention of Aniline and DMA*

	Redox Reagent Injection	PPCl		PPDS/Si
		Aniline k′	DMA k′	DMA k′
0.1M Na_2SO_3	0	1.8	1.7	4.7
	100	1.7	1.3	3.9
	200	1.0	0.6	3.5
	300	0.8	0.5	3.0
0.1M $FeCl_3$	40	2.7	2.2	3.4
	80	3.0	2.3	2.8
	120	---	---	2.4

* Mobile phase: 40% MeOH/H_2O for aniline and 60% MeOH/H_2O for DMA, at 1 mL/min.

Chemical Composition of Column Packings

The elemental composition of the polymer layer coated on the surface of silica particles for polypyrrole chloride (PPCl/Si) and polypyrrole dodecylsulfate (PPDS/Si) is presented in Table 1.

The mole ratio of N:Cl in PPCl/Si is 2.1 : 1.0, which suggests that one Cl^- counterion is associated with 2.1 monomer units. This result is lower than the expected value, which is normally in the range 3-4.[22] It has been reported, previously, that this probably is due to the fact that $[Fe(Cl)_4]^-$ was incorporated

as a counterion.[23,24] During PPyDS/Si preparation, both chloride and dodecylsulfate (DS^-) counterions were incorporated into the polymer matrix. The mole ratio of N : (Cl + DS) is 2.04 : 1.0, which indicates that every 2 pyrrole monomer units were associated with either one Cl^- or DS^- counterion.

Retention Behaviour of Benzene and Derivatives

The effect of chemical manipulation on PPCl/Si with the redox reagents upon the retention behaviour of benzene and toluene was investigated. No effect was found. Benzene and toluene are considered to be non-polar compounds. Their separation, in liquid chromatography, is therefore mainly determined by hydrophobic interaction.

In addition, benzene as an aromatic compound, is an electron donor through the π system. So also is toluene, which is even more hydrophobic due to the presence of the methyl group. Their retention on the column remained essentially unaffected by this redox manipulation. Similar results were obtained for PPDS.

Different results were obtained with aniline and DMA as test studies. The effect of redox reagent treatment of PPCl/Si on retention behaviour is presented in Table 2. The retention of these compounds decreased after the column was treated with the reductant and then increased even beyond the original retention values after the column was in contact with the oxidant. Aniline and DMA are amines which have a tendency to share their unpaired electrons; hence, they are electron donors through their lone-paired electrons.

The retention behaviour of aniline and DMA, after the column was treated with the reagents, indicated that such treatment changed the ability of the column to undergo electron donor-acceptor (EDA) interactions through the unshared paired electrons. The increased retention after reoxidation suggests that the polymer was then in a higher oxidation state than the rest potential that resulted in the initial retention values.

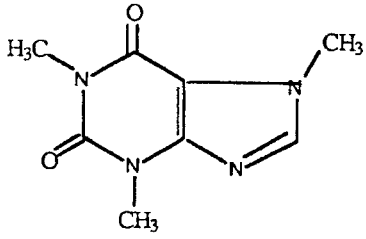
The possibility that DS^- counterions were expelled upon reduction and gradually leached out from the PPDS/Si column during the washing and contact with the mobile phase was indicated by the retention behaviour of aniline on this column. After the second run of column treatment with the reductant, the peak intensity of this analyte was lower and needed more injections to obtain a steady peak height. Although it eluted faster, it was clear that some part of the aniline was irreversibly adsorbed, which suggested that some reactive sites on the

surface of silica had became more accessible. This might also be due to irreversible changes in the polymer during treatment. Attempts were made to elute aniline after the column was reoxidised. After several injections, only very small peaks with irregular shapes were observed. This made it difficult to measure the retention times.

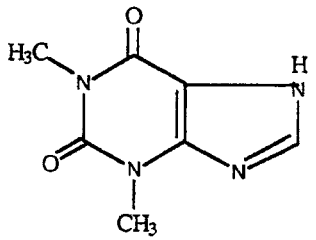
The retention behaviour of DMA on PPDS/Si is presented in Table 1. It has been observed previously that DS^- counterions intercalated in the polypyrrole stationary phase enhanced the capability of the column for hydrophobic interaction with DMA, as well as improving the selectivity.[24] As shown in Table 1, interaction reversibility, as observed on polypyrrole chloride column, is not shown here. Instead, the retention tended to decrease constantly as the column was subjected to reduction-oxidation treatments. This phenomenon seemed to suggest that, again, DS^- counterions were leaching out slowly during the course of chromatographic measurements. This process probably compensated or offset any effect from redox manipulation.

The effect of chemical manipulation on the chromatographic properties of the polymers was also tested using phenol as the test compound. Because phenol is a proton donor compound, the effect of the treatment on the proton-accepting ability of the polymers could be examined. It was found that the retention of phenol on both columns was essentially unaffected by the exposure of the coated polymers to the redox reagents, which indicated that its proton-accepting ability was not disturbed.

Retention Behaviour of Basic Drugs



caffeine



theophylline

The effectiveness of the chemical manipulation on PPCl/Si was also tested with the elution of theophylline and caffeine (Table 3). It is shown that this redox manipulation affected theopylline more than caffeine. These compounds have very similar molecular structures (see below), yet they have quite different basicities, which would reflect their capability of interacting through EDA interactions.

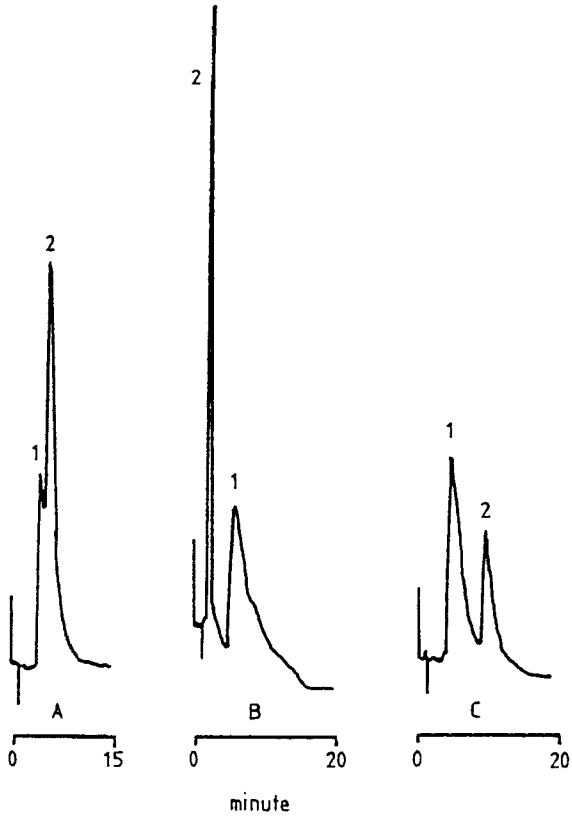


Figure 2. Effect of the injected redox reagents into PPCl/Si column on the chromatographic separation of theophylline (1) and caffeine (2).
Mobile phase : 65 % MeOH / H_2O at 1 ml / min. A: before the reagents were injected; B: after 1.0 mL 0.1 M Na_2SO_3 was injected; C: after 0.8 mL 0.1 M $FeCl_3$ was injected (following step B).

Theophylline is a stronger base (pK_a = 3.5) than is caffeine (pK_a = 0.6). This suggests that theophylline tends to donate its unshared paired electrons more readily, and is, hence, more sensitive to the changes in the EDA interactions capability of the column. If this argument holds true, it confirms, further, that the redox treatment did change the properties of the stationary phase to some degree. Upon reduction, the retention of theophylline decreased

and went to the original value upon reoxidation. The improvement in selectivity of the column, upon reduction, is more clearly demonstrated in the chromatograms (Figure 2).

The prediction that the presence of DS^- counterions would induce different kinds of interactions with the analytes was not obvious in experiments involving theophylline and caffeine. From the retention point of view, both analytes responded to redox manipulation in a parallel way; there was no essential improvement in selectivity. The retention behaviour of theophylline on the PPDS/Si column was different from that observed with the PPCl/Si column (Figure 3). As can be seen, column reoxidation did not restore the separation profile. All the results obtained from this column seemed to suggest that the use of redox manipulation to modify the properties of the stationary phase was not effective. Perhaps it changed to some degree, but then it was offset by the possible irreversible change in the polymer backbone on exposure to high pH. The possibility that Na^+ ions were incorporated, due to the treatment of the column with the reductant, should also be taken into account. The presence of these cations might induce different behaviour of the polymer when interacting with the test compounds.

Retention Behaviour of Amino Acids

In this study, two amino acids, i.e., L-tyrosine (Tyr) and L-tryptophan (Trp), were used as the probes for the following reasons:

1. Their isoelectric points (pI) are similar i.e., 5.67 and 5.88 for Tyr and Trp, respectively, which makes it easier to adjust the pH.

2. Both have aromatic rings, which makes it easy to detect by a UV detector without derivatisation.

3. Their hydrophobicities are quite different from each other, with Tyr being less hydrophobic than Trp,[25] which would result in different degrees of interaction with the polymeric phase.

Depending on the pH of the solution, the charges on the amino acids can be manipulated as illustrated below. In this work, the pH's of the buffer components in the eluent were 3.8 and 7.4, which were well apart from the pI values of the amino acids.

The effect of the injection of the Na_2SO_3 solution into the PPCl/Si column on the retention behaviour of Tyr and Trp is illustrated by the chromatograms in Figures 4 and 5a. At pH 3.8, the amino acids are positively charged. The side

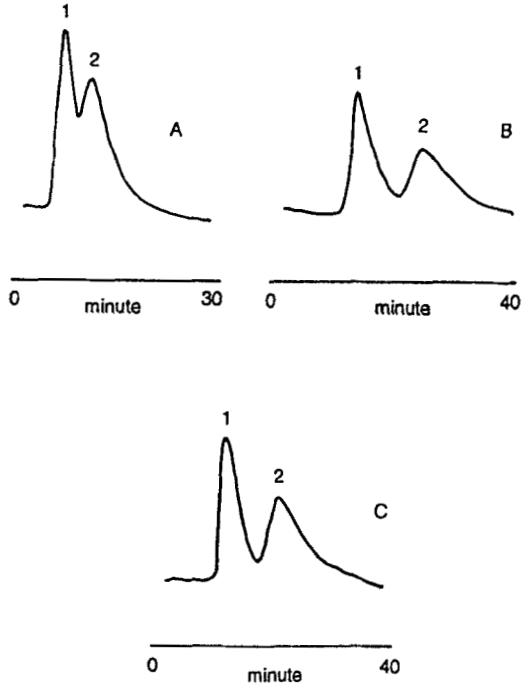
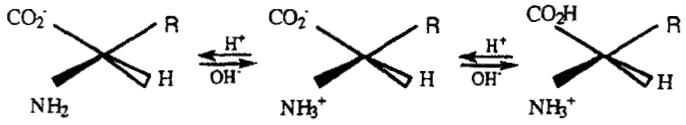


Figure 3. Effect of the injected redox reagents into PPDS/Si column on the chromatographic separation of theophylline (1) and caffeine (2). Mobile phase : 60 % MeOH/H_2O at 1 mL / min. A: before the reagents were injected; B: after 1.2 mL 0.1 M Na_2SO_3 was injected; C: after 1.0 ml 0.1 M $FeCl_3$ was injected (following step B).

chains of the amino acids, here, are hydrophobic in character. The chromatograms obtained suggest that, after the exposure of the polymeric phase to the reductant solution, the interaction between the amino acids and the phase became stronger due to increased hydrophobic interactions.



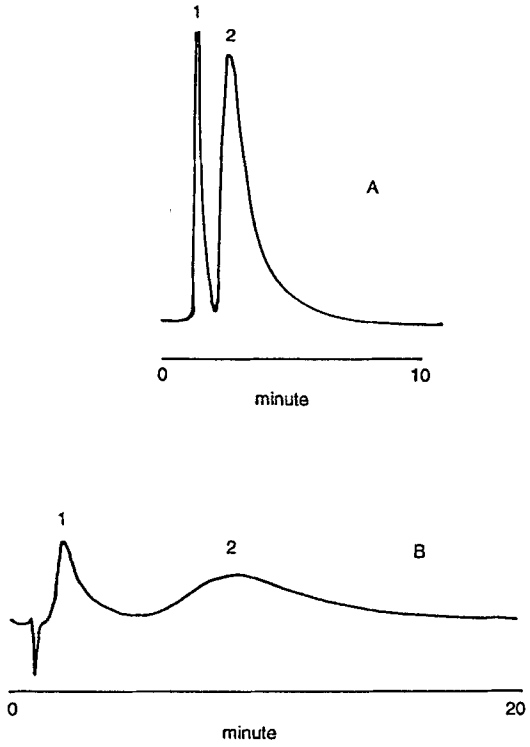


Figure 4. Chromatographic separation of tyrosine (1) and tryptophan (2) on PPCl/Si before (A) and after (B) the introduction of 1.0 mL 0.1 M Na_2SO_3 into the column. Mobile phase: 30 % MeOH / acetate buffer pH 3.8 at 1 mL/min.

The rationalization of the phenomenon is that, after the polymeric phase was exposed to the reagent, it was reduced so that its positive charges diminished, which resulted in the decrease of the repulsion effect between the polymeric phase and the amino acids.

At higher buffer pH (7.4) the amino acids should have net negative charges, which could enhance the electrostatic attraction between these and the polymeric phase.

The electrostatic interaction in combination with hydrophobic interactions resulted in longer retention times.

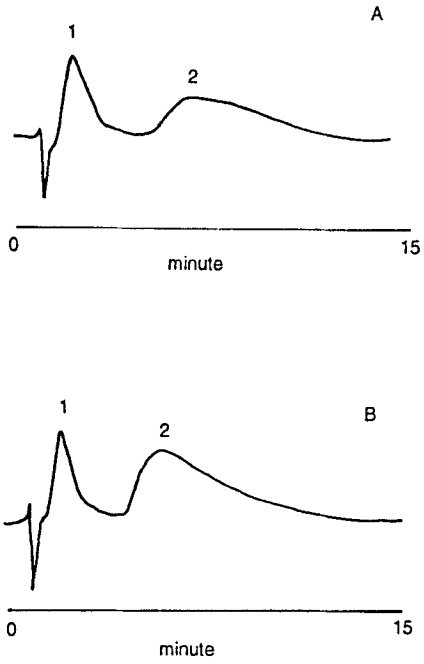


Figure 5a. Chromatographic separation of tyrosine (1) and tryptophan (2) on PPCl/Si before (A) and after (B) the introduction of 1.0 mL 0.1M Na_2SO_3 into the column. Mobile phase : 30 % MeOH/Tris-HCl, pH 7.4, at 1 mL/min.

A noticeable effect can be observed after the introduction of Na_2SO_3 solution, where the retention of the amino acids decreased. This effect was more marked for Trp, which is more hydrophobic than Tyr. The decrease in retention of the amino acids is attributed to reduction of the polymeric phase, removing the positive charges on the polymer backbone.

The effects of chemical manipulation on the chromatographic behaviour of the amino acids, using PPDS/Si, are illustrated by the chromatograms in Figures 5b and 5c. As can be seen in Figure 5b, the introduction of Na_2SO_3 solution into the column before the injection of the test compounds resulted in dramatic changes to the retention profile of the amino acids at low pH. Similar behaviour, as observed on PPCl/Si, occured on this column. On the original column, where the polymeric phase was positively charged, the electrostatic repulsion between this phase and the amino acids took effect, lowering the

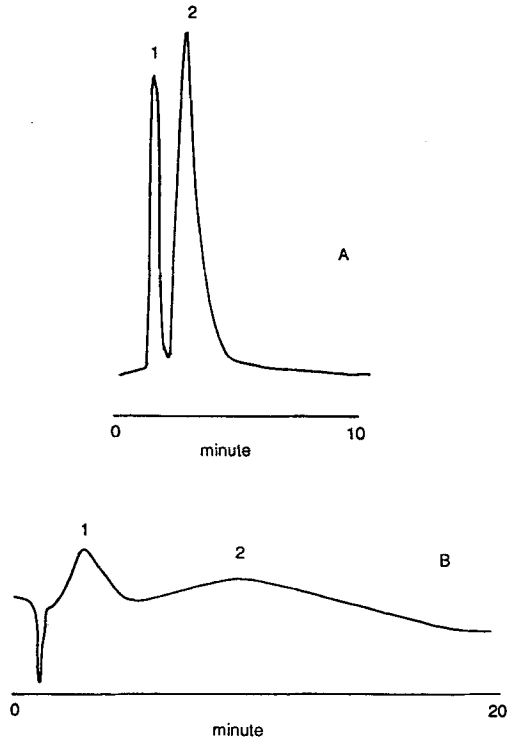


Figure 5b. Chromatographic separation of tyrosine (1) and tryptophan (2) on PPDS/Si before (A) and after (B) the introduction of 1.2 mL 0.1 M Na_2SO_3 into the column. Mobile phase : 30 % MeCN / acetate buffer, pH 3.8, at 1 mL/min.

retention time. Upon reduction with Na_2SO_3 solution, the positive charges on the polymeric phase are reduced. Because DS^- counterions had low mobility, which rendered them hard to expel on reduction,[17-19] the Na^+ cations could well be incorporated to compensate the negative charges of the counterions. When the amino acids were passing through the chemically treated column in low pH buffer, two different interactions could take place, i.e., cation-exchange and or hydrophobic interactions. The positively charged amino acids exchanged with sodium ions, a process that would be accompanied by hydrophobic interactions. As can be seen in Figure 5b, the amino acids were then more strongly retained.

In Figure 5c, the effect of chemical manipulation of PPDS/Si on the retention of the amino acids at neutral pH is shown. Under these conditions, the amino acids have a negative net charge, encouraging stronger interactions with

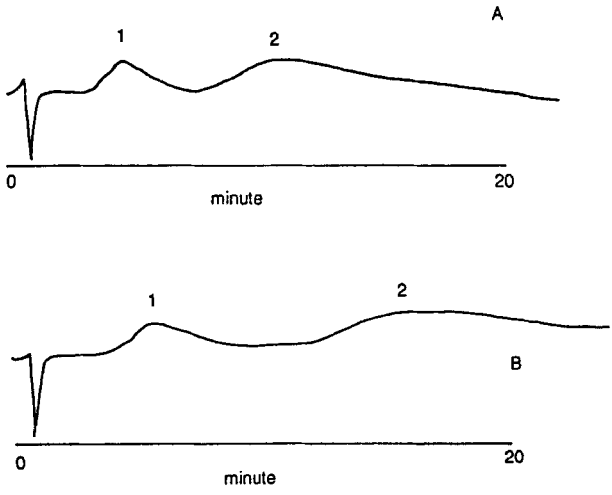


Figure 5c. Chromatographic separation of tyrosine (1) and tryptophan (2) on PPDS / Si before (A) and after (B) the introduction of 1.2 mL 0.1 M Na_2SO_3 into the column. Mobile phase : 30 % MeCN / Tris-HCl, pH 7.4, at 1 mL / min.

the untreated positively charged polymeric phase. After the column was treated with Na_2SO_3 solution, it was expected that the interaction between the polymeric phase and the amino acids would decrease. However, this was not observed. Instead of becoming weaker, the interactions were even stronger. The reason behind this phenomenon was not immediately obvious; the possibility of the inclusion of Na^+ was probably responsible for this behaviour. Perhaps the inclusion of these positively charged ions into the polymer increased the attractive interactions between the polymer and the negatively charged amino acids.

Reversibility of The Effect of The Chemical Treatment

It has been demonstrated, previously, that chemical treatment of the polypyrrole chloride column with redox reagents alters the properties of the polymeric phase, as revealed by the elution behaviour of theophylline and caffeine. The reversibility of this treatment was then considered. It is commonly believed that the oxidation state of conductive polymers, such as

Table 3

Effect of Redox Treatment of PPCl/Si on the Retention of Caffeine and Theophylline*

	Redox Reagent Injection (μL)	k′ Caffeine	k′ Theophylline
0.1M Na_2SO_3	0	2.5	1.7
	100	2.4	1.1
	200	2.6	0.8
	300	2.8	0.2
0.1M $FeCl_3$	100	2.3	1.6
	200	2.1	1.6

* Mobile phase: 60% MeOH/H_2O at 1 mL/min.

Table 4

Retention of Caffeine and Theophylline on PPCl/Si as a Function of the Treatment of the Column with Redox Reagent*

	k′ Caffeine	k′ Theophylline
Frc	2.6	2.2
red_1	2.7	0.1
oxd_1	2.3	2.0
red_2	2.4	0.1
oxd_2	2.1	1.8

*60% MeOH/H_2O at 1 mL/min. Frc: fresh column; red: after column was treated with 0.1M Na_2SO_3; oxd: after column reoxidation with 0.1M $FeCl_3$.

polypyrrole, can be reversibly altered by reduction-oxidation processes either chemically or electrochemically. In the following discussion, the reversibility was tested chromatographically and determined by the variation in the capacity factors observed for theophylline and caffeine.

Table 4 shows the result of reversibility test on PPCl/Si. The retention of theophylline and caffeine was first measured on the fresh column and remeasured after the column was alternately treated by the injection of Na_2SO_3

Table 5

Retention of Caffeine and Theophylline on PPD/Si as a Function of the Treatment of the Column with Redox Reagent*

	k′ Caffeine	k′ Theophylline
Frc	7.1	4.3
red$_1$	18.3	9.7
oxd$_1$	17.7	9.4
red$_2$	17.1	8.9
oxd$_2$	16.6	8.6

*60% MeOH/H_2O at 1 mL/min. Frc: fresh column; red: after column was treated with 0.1M Na_2SO_3; oxd: after column reoxidation with 0.1M $FeCl_3$.

and $FeCl_3$ solution. As can be seen, the reversibility of the effect of the chemical manipulation was verified. The retention of theophylline decreased to almost zero upon treatment with the reductant and back to almost normal following the treatment of the column with the oxidant. An opposite trend was observed for caffeine. The reversible behaviour observed with PPCl/Si was not observed with PPDS/Si (Table 5). This does not necessarily mean, however, that oxidation-reduction processes did not occur. As revealed by the retention behaviour of Tyr and Trp in the previous discussion, the lack of the fluctuation in retention on this column for the test compounds might be due to the different mechanism in the reduction-oxidation processes.

In this study, it was unclear which mechanism was more dominant. It could be through either an electron transfer or a protonation-deprotonation process. Both of these processes could lead to an increase or decrease of the conductivity of the polymer which, in turn, would lead to interaction with certain test compounds in different ways. Furthermore, the occurence of irreversible changes was also possible.

CONCLUSION

An examination of the effect of the exposure of polypyrrole chloride and polypyrrole dodecylsulfate to redox reagents has been carried out. It was found that the exposure brought changes in the properties of the polymers investigated

as indicated by the chromatographic elution behaviour of the test compounds in the columns packed with the polymer-coated packing materials. It was observed that the effect was more pronounced on the packing prepared from polypyrrole chloride. The changes observed on this material seem to be reversible.

The similar variation in electrode potential measured on polypyrrole chloride-coated platinum, that resulted from the exposure of the electrode to electrochemical and chemical redox manipulation, might suggest that reduction-oxidation process did occur during chemical exposure. Further investigation, however, might still be needed to be certain that other processes such as protonation-deprotonation were not involved.

The results of the study also suggest that, if the polypyrrole chloride polymer is used as a stationary phase for chromatography, the treatment with redox reagents would improve the column selectivity by exploiting the differences in the solutes' capability for producing electrostatic or charge-transfer interactions.

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