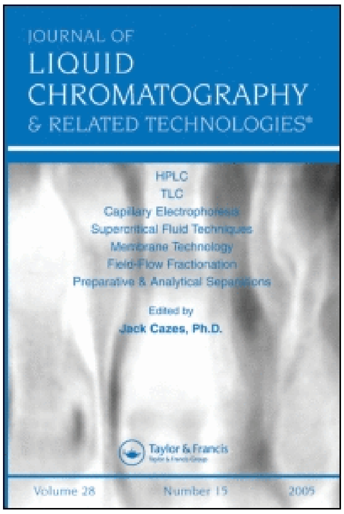

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SEPARATION OF THE UREA PIPERAZINE DERIVATIVES OF POLYISOCYANATE MONOMERS AND PREPOLYMERS BY NORMAL PHASE CHROMATOGRAPHY

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ABSTRACT

A normal-phase high-performance liquid chromatographic method is described for the determination of aliphatic and aromatic poly isocyanate monomers or prepolymers after derivatization with 1-(2-methoxyphenyl) piperazine.

The separation of 2,4 TDI, 2,6 TDI, HDI and MDI derivatives was performed with 5 and 10 µm cyan-amino bonded silica columns, under isocratic conditions and with ultra-violet detection. The same elution conditions were used for the resolution of several commercial isocyanate prepolymer derivatives, in reasonable analysis times.

INTRODUCTION

Polyfunctional isocyanates are widely used in the production of polyurethane foams, coatings, elastomers and adhesives. Because these chemicals are known to cause skin and respiratory tract irritation, their determination in air or in commercial products has been the subject of many studies [1-2-3-4].

The introduction of high performance liquid chromatography has led to the development of various sensitive and selective methods for the measurement of isocyanates [1-5-6-7-8-9-10]. One of the most recent procedures uses the 1-(2-methoxyphenyl)piperazine as a chromophor and electrophor- derivatizing reagent, and the analysis of urea derivatives was carried out on the reversed phase system with ultraviolet and/or electrochemical detection to identify isocyanate-derived HPLC peaks [8-11].

Recently, a normal-phase HPLC method with a cyan-amino column was described to analyse airborne TDI after its derivatization with 1-(2-methoxyphenyl)piperazine [12]; but no normal-phase method has been described, so far, to separate piperazine prepolymer derivatives.

As an extension of this previous work, we used the normal-phase HPLC method to separate and resolve four isocyanate monomers, as well as several commercial isocyanate prepolymers. The separation of HDI, MDI, 2,4 and 2,6 TDI was optimized with three batches of bonded silica, under isocratic conditions.The ability of the method to separate and analyze the monomer and prepolymer in commercial hardeners was illustrated.

MATERIALS AND METHODS

Chemicals

Toluene diisocyanate (2,4/2,6 TDI), 1,6 hexamethylene diisocyanate (HDI) and 4,4'-diphenylmethane diisocyanate (MDI) were purchased from Merck (Darmstadt), and vacuum distilled before use. 2,6 toluene diisocyanate and 1-(2-methoxyphenyl)piperazine were purchased from Aldrich, and were used without further purification. The following isocyanate prepolymers were used : Desmodur N and Desmodur 3390 (HDI-based prepolymers ; BAYER), Desmodur R and RF, DESMODUR L (TDI-based prepolymer ; BAYER) and Desmodur HL (TDI/HDI-based prepolymer ; BAYER). Solvents were purchased from Merck, and were of HPLC grade.

Chromatographic apparatus

Analyses were carried out with a VARIAN (Series 5000) chromatograph, equipped with a RHEODYNE injection valve (series 7125), a 10 µL sampling loop, and a PHILIPS Pye Unicam 4020 variable wave-lengh UV detector set at 254 nm. The columns used were stainless-steel tubing, of 25cm in length and of 4.6 mm ID, slurry-packed at 6000psi (using 2-propanol/95% ethanol/toluene 1/1/1 vol/vol) with cyan-amino bonded silica (PARTISIL PAC 5 µm or/and 10 µm ; WHATMAN).

Mobile phase

The following optimized mobile phases were used: isooctane/CH_2Cl_2/MeOH (60/34/6) for the first 5 µm silica batch, isooctane/CH_2Cl_2/MeOH (70/20/10) or isooctane/CH_2Cl_2/MeOH/ ETOH (72/15/10/3) for the second 5 µm silica batch, and isooctane/CH_2Cl_2/MeOH (73/15/12) for the 10 µm silica batch. They were de-aerated with helium (10 min) and pumped at a flow rate of 1mL/min.

Piperazine derivatives and standard solutions

The derivatization was performed according to the method of PURNELL et al. [8]. 10^{-3}mole of isocyanate monomer or prepolymer was dissolved in 20 mL of dry-suitable solvent (hexane, toluene, ethyl acetate), and a solution (5 mL) of excess 1-(2-methoxyphenyl)piperazine (6-12 10^{-3}mole) depending on the number of NCO functions, was added, and the mixture was shaken for 30 min. The derivative precipitated down as white crystals, which were collected on frit-glass and washed several times with a suitable solvent (hexane, toluene or ethyl acetate) to remove the excess reagent. The derivatives were soluble in THF, MeOH or CH_3CN ; 50 mg were dissolved in 100 mL of an adequate solvent and suitable aliquots of these solutions were diluted in CH_3CN or THF to give a series of standard solutions.

Procedure for the treatment of commercial polyurethane prepolymers

The isocyanate prepolymers (50 mg) were dissolved in 5 mL of dry THF, then a solution of excess 1-(2-methoxyphenyl)piperazine (200 mg) in THF (5 mL) was added. The solution was shaken for 30 min and if precipitation occurred, a quantity of THF was added until dissolution. Then acetic anhydride (10 µL) was added to 1 mL of the sample solution to destroy the excess of reagent, and a series of dilutions was performed in CH_3CN or THF.

Prior to analyses, residual acetic anhydride can be neutralized with one drop (20µL) of methanol.

Procedure for the treatment of air sampling

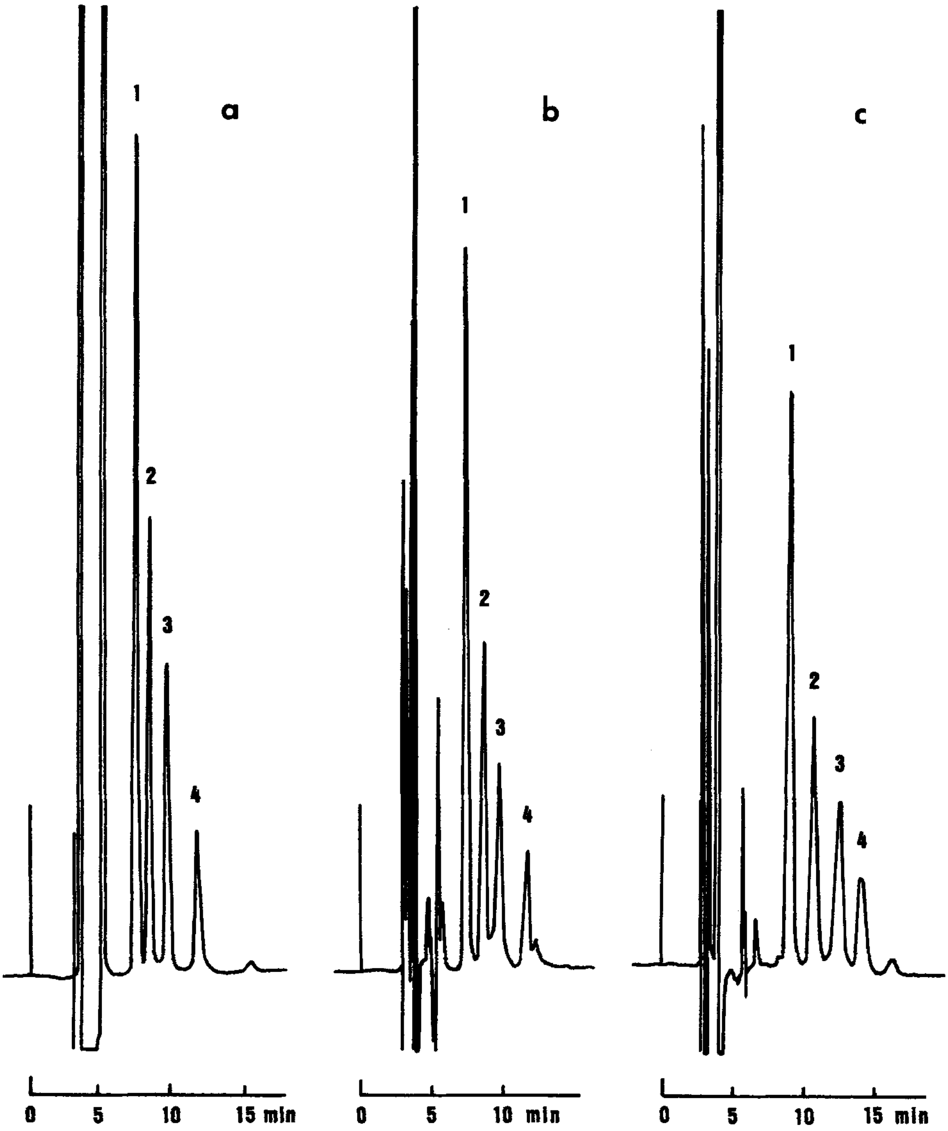
The sampling method and the treatment of airborne TDI specimens have been detailed [12]. Sampling of other isocyanates was performed with a glass-bubbler containing 10 mL of 2 10^{-4}M solution of 1-(2-methoxyphenyl)piperazine in toluene, as previously described [1]. After sampling, the toluene was evaporated under a stream of nitrogen, or in a rotary evaporator at 50°C, and the residue was dissolved in 3 mL of CH_3CN or THF. All samples were treated as follows prior to their injection : 5 µL of acetic anhydride were added to 0.5 mL of each sample to convert the unreacted amine to its acetyl derivative, and residual acetic anhydride was destroyed with 10 µL of methanol.

RESULTS AND DISCUSSION

Chromatographic studies of isocyanate monomers

The most common isocyanate monomers used in industry are (2,4 and 2,6) TDI, MDI and HDI; their separation under the isocratic mode and within short time elution is relevant for a rapid recognition and analysis of these compounds. For this purpose, the HPLC conditions were optimized with three batches of cyan-amino bonded silica gel (Fig. 1).

For one batch, complete separation ($R_S > 1.5$) of the standard urea derivatives of the four isocyanates could be achieved in less than twelve minutes with a ternary mobile phase containing isooctane (60), dichloromethane (34) and methanol (6) (Fig. 1a). In order to select the optimum ternary mobile phase mixture, a study of the k'values was done by varying the solvent composition (Fig 2). The elution order of the MDI and 2,6 TDI can be reversed by changing the proportion of isooctane or CH_2Cl_2 in the mobile phase, while no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elution order inversion occurred with variation of the methanol content.

With the second batch, separation was achieved with the following solvent systems : isooctane (72)dichloromethane (15)methanol (10) ethanol (3) (Fig. 1b) or isooctane (70)dichloromethane (20)methanol (10) (Fig. 3).

The addition of ethanol in the mobile phase improved slightly the resolution between HDI and 2,4 TDI derivative peaks.

With the third batch (cyan-amino 10 µm), the adequate solvent system consisted of isooctane (74) dichloromethane (12) methanol (14) (Fig. 1c).

The amine reagent was strongly adsorbed on silica, which may cause tailing and interference with the urea-derivative peaks (Fig. 3b) : consequently, the excess reagent present after derivatization must be destroyed with acetic anhydride, so that its acetyl derivative is

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Figure 1 :

Separation of standard 1-(2-methoxyphenyl)piperazine derivatives on cyan-amino columns (4.6 x 250 mm).

Flow rate : 1 mL/min, injection volume 10 µL, U.V. : λ = 254 nm and 0.04 a.u.f.s.

a) 5 µm silica batch n°1
eluent : isooctane, CH_2Cl_2, MeOH (60/34/6)

b) 5 µm silica batch n°2
eluent : isooctane, CH_2Cl_2, MeOH, EtOH (72/15/10/3)

c) 10 µm silica batch
eluent : isooctane, CH_2Cl_2, MeOH, (75/13/12)

1 HDI (50 ng); 2 2,4 TDI(8.9 ng); 3 MDI (7 ng); 4 2,6 TDI (8.7 ng)

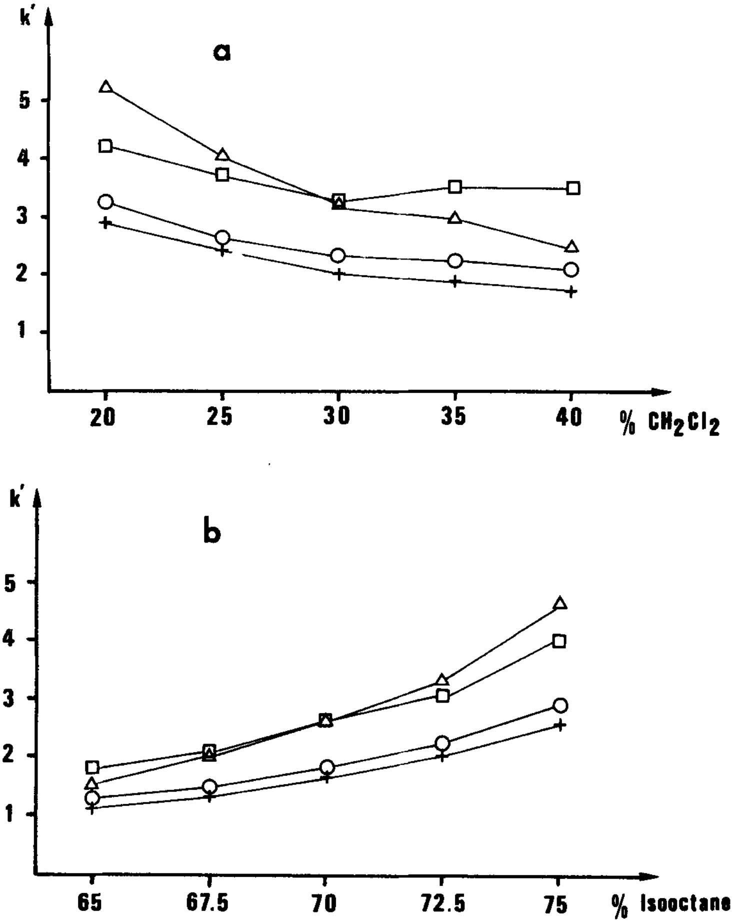


Figure 2 :

Relationship between capacity factor, k', for urea derivatives and % solvent C content of the mobile phase. Cyan-amino column (4.6 x 250mm) 5 µm silica batch n°1, flow rate 1mL/min, injection volume 10 µL.

a) Solvents : A isooctane, B MeOH, A/B (10/1), C CH_2Cl_2
b) Solvents : A CH_2Cl_2, B MeOH, A/B (2.5/1), C isooctane
c) Solvents : A isooctane, B CH_2Cl_2, A/B (6/3.5), C MeOH

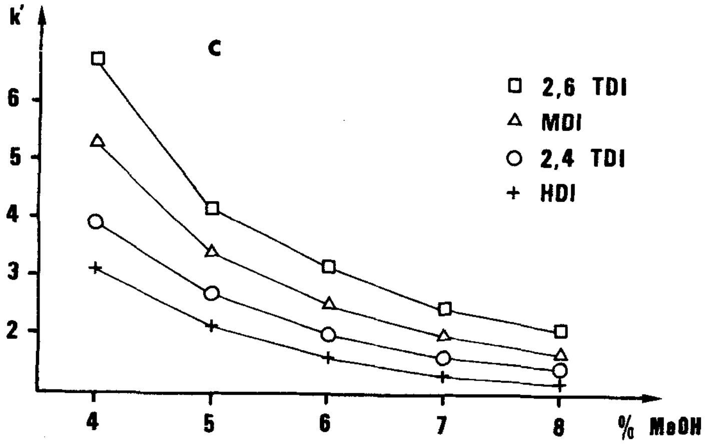
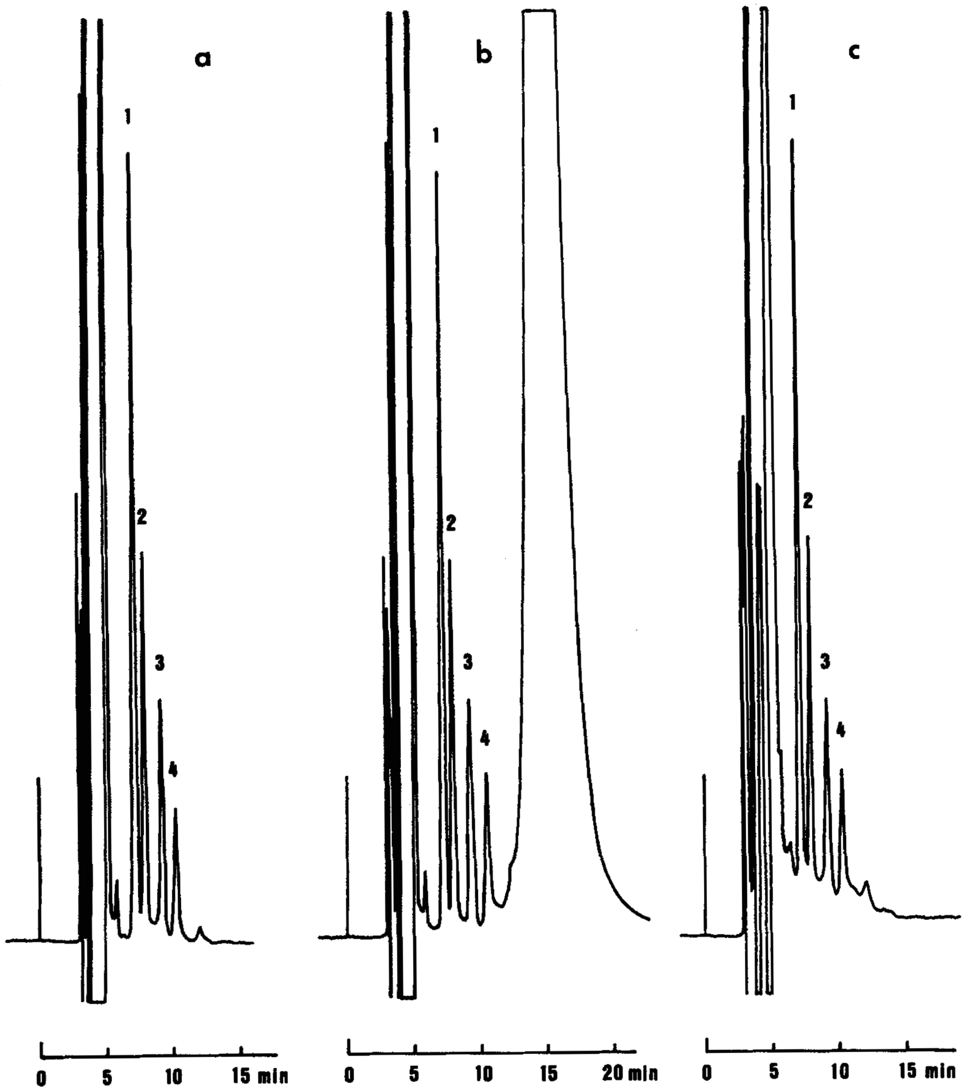


FIG. 2 (continued)

eluted in the solvent front (Fig. 3c). This acetylation reaction adds a further derivatization step without any change in analysis time and detection limits. 1% triethylamine has been used in the mobile phase to reduce the influence of the residual silanol groups and to protonate the amine reagent and reduce its retention [13]. But, with the cyanamino silica column, this method disturbed significantly the retention times of isocyanate derivatives and the column properties.

Chromatographic studies of isocyanate prepolymers

The separation of the main components of a commercial prepolymer is required for the identification and quantification of prepolymeric and residual monomeric isocyanates, which is important for both quality control and safety. The separation of the piperazine urea derivatives of isocyanate prepolymers has been performed previously [2-11] by reversed-phase chromatography; however, the use of a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complementary method may be useful to improve the identification when that of the peak is ambiguous.

In this respect, the normal-phase HPLC method proposed here is suitable, and Fig. 4-5-6 show chromatograms of the urea derivatives of Desmodur N, 3390, R, RF, L and HL. Idealised formulae of the parent-prepolymers are shown in Fig. 7. The method is routinely used in our laboratory for the analysis of commercial polyurethane preparations (hardeners, paints ...), and for the identification and quantification of the isocyanate oligomers and residual isocyanate monomers, in these commercial products.

So, sample solutions of commercial preparations of Desmodur N and Desmodur 3390 were derivatized and compared with standard solutions prepared from precipitated urea derivatives. The sample solutions gave a similar pattern of peaks to the standard, and contained approximately the same percentage of each peak and the same amount of each product, indicating that the main oligomer coumpounds were eluted from the column.

Figure 3 :

Separation of piperazine derivatives and piperazine reagent on the cyan-amino column (4.6 x 250 mm) 5 µm silica batch n°2.
Flow rate : 1 mL/min, injection sample 10 µL ; U.V. : λ = 254 nm and 0.04 a.u.f.s. eluent : isooctane, CH_2Cl_2, MeOH (70/20/10)

a) piperazine derivatives standard
 1_HDI (50 ng) ; 2_ 2,4 TDI (8.9 ng) ; 3_ MDI (7 ng) ;
 4_ 2,6 TDI (8.7 ng)

b) piperazine derivatives standard with excess piperazine reagent (4000 ng) ; no acetic anhydride added

c) same sample as 3b ; acetic anhydride added

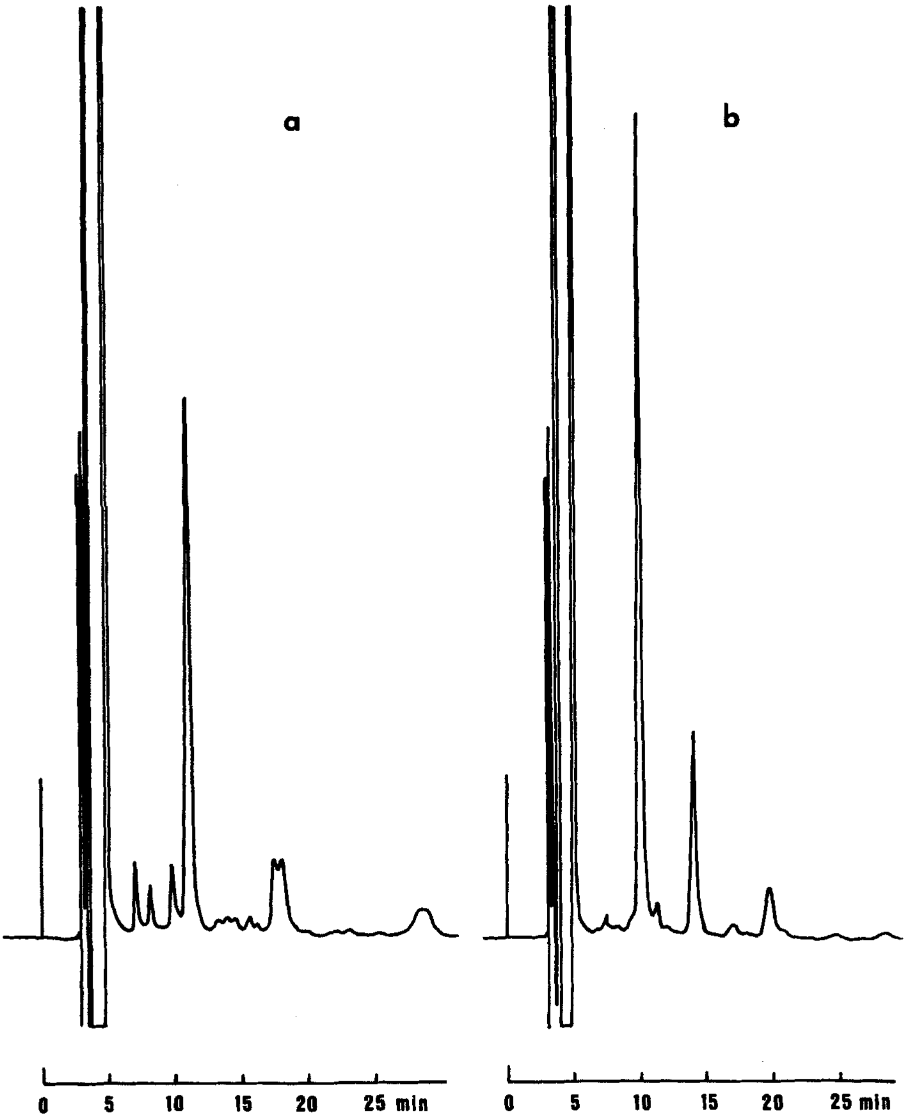


Figure 4 :

Chromatograms of HDI based prepolymer urea derivatives.
Cyan-amino column (4.6 x 250 mm) 5 µm silica batch n°2 ;
flow rate : 1 mL/min, injection sample 10 µL ; U.V. : $\lambda = 254$ nm and 0.04 a.u.f.s. ; eluent : isooctane, CH_2Cl_2, MeOH (70/20/10)

a) Desmodur N_{75} 22.1 µg/mL (derivative 48.8 µg/mL)
b) Desmodur N_{3390} 18.2 µg/mL (derivative 39.1 µg/mL)

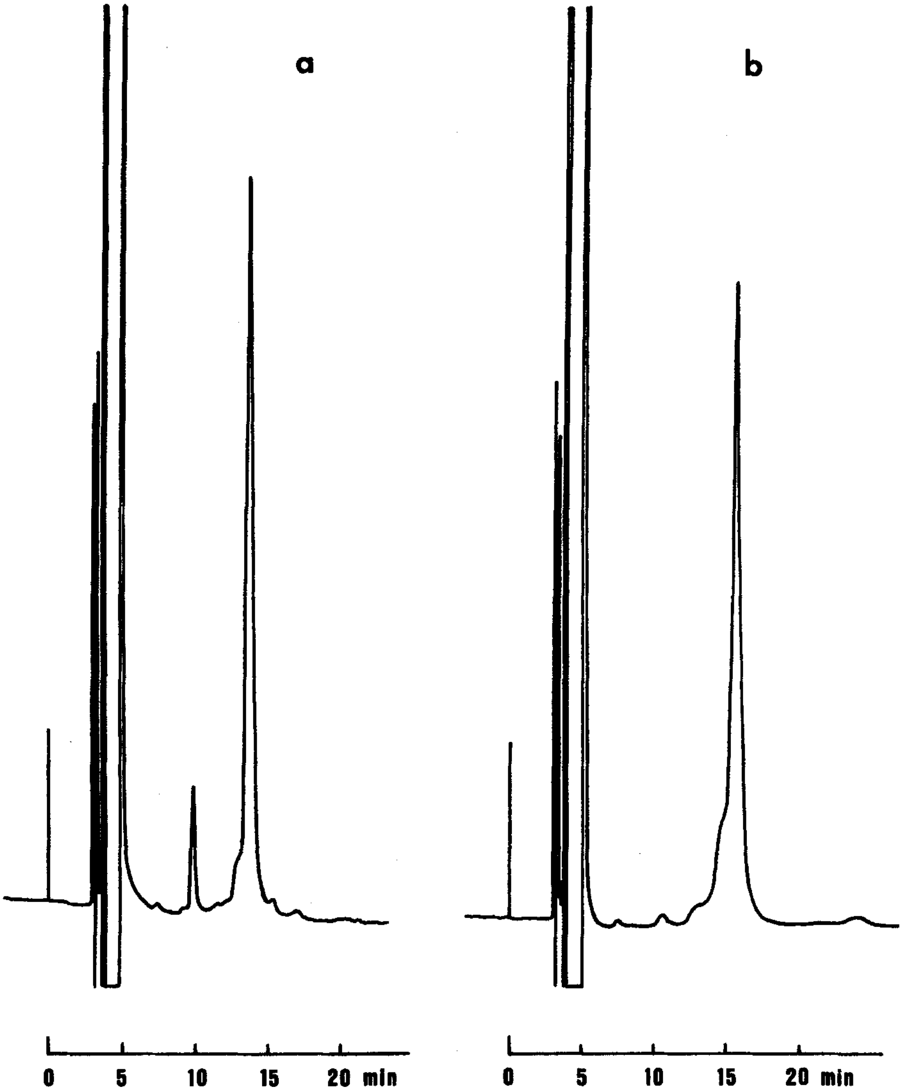


Figure 5 :
Chromatograms of Desmodur R and RF urea derivatives.
Same conditions as in Fig. 4

a) Desmodur R 5.64 µg/mL (derivative 14.5 µg/mL)
b) Desmodur RF 4.6 µg/mL (derivative 10.3 µg/mL)

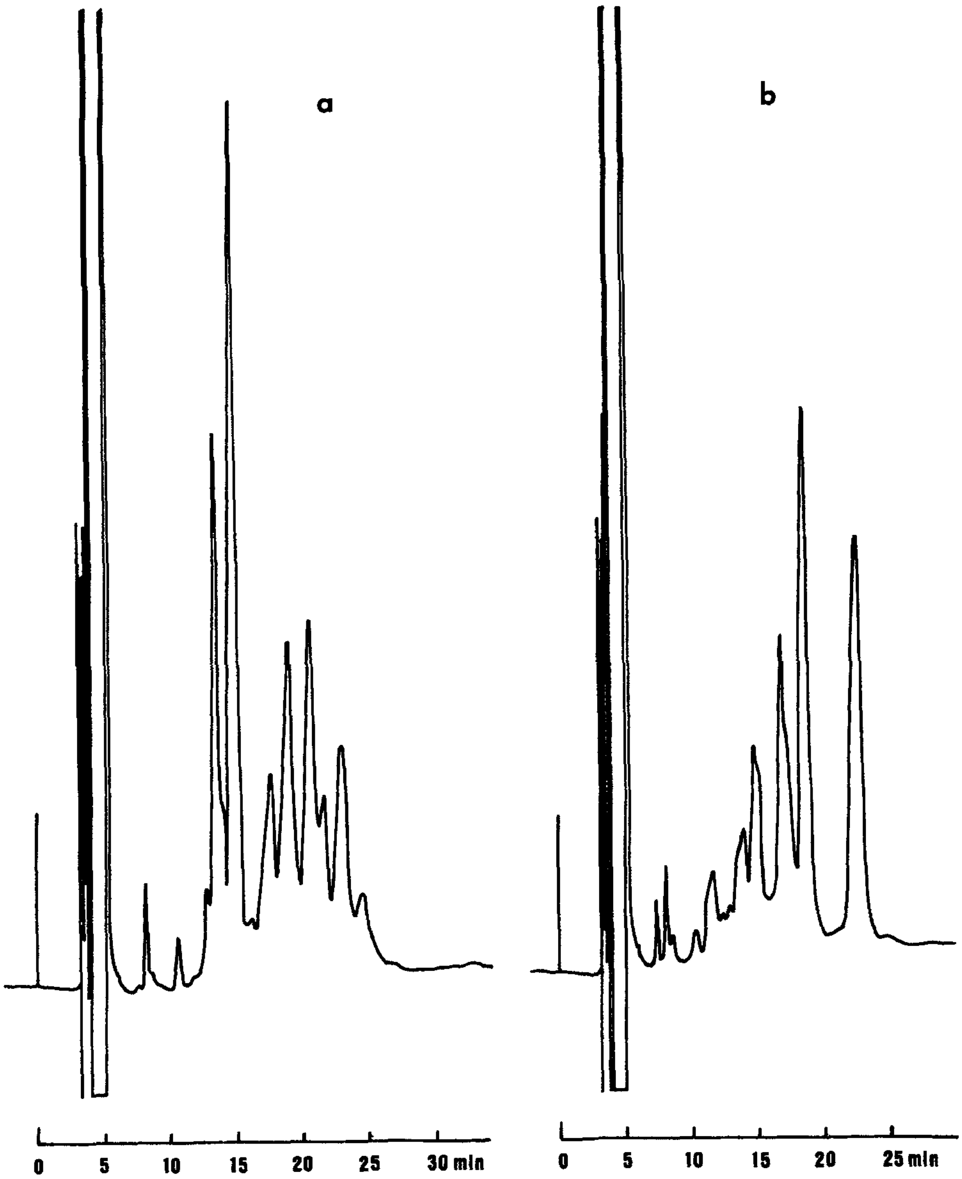
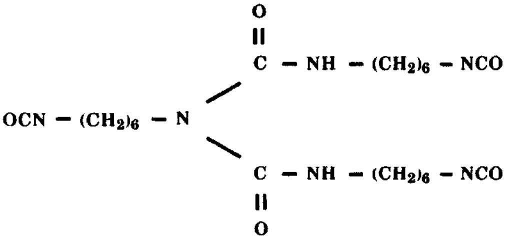
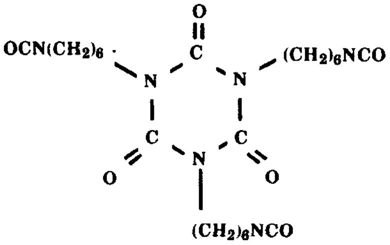


Figure 6 :
Chromatograms of TDI and TDI/HDI based prepolymer urea derivatives.
Same conditions as in Fig. 4

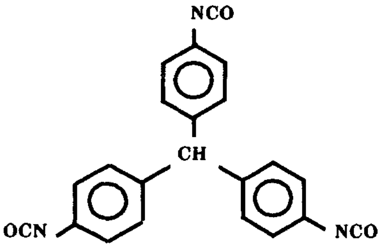
a)	Desmodur L	224 µg/mL (derivative 390 µg/mL)
b)	Desmodur HL	199 µg/mL (derivative 377 µg/mL)



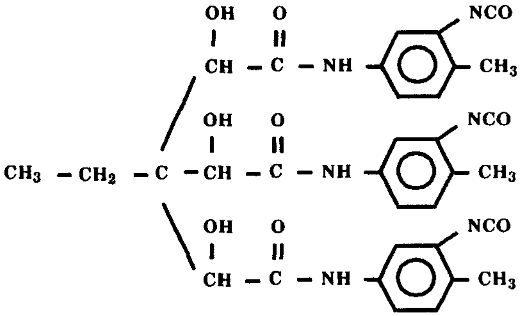
DESMODUR N 75



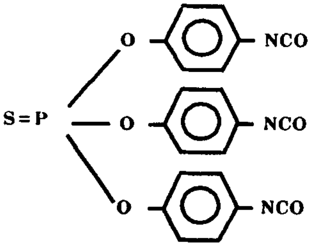
DESMODUR N 3390



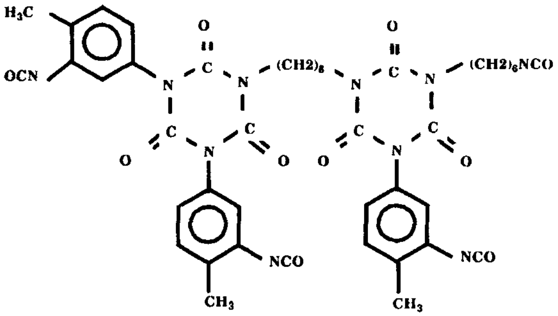
DESMODUR R



DESMODUR L



DESMODUR RF



DESMODUR HL

Figure 7 :

Idealised formulae of the prepolymers N 75, N 3390, R, RF, L and HL.

Many analysis examples showed that the use of normal-phase chromatography was more convenient than reversed-phase chromatography for routine analyses.
Firstly, elution conditions of prepolymer and monomer isocyanate derivatives are similar, so no change of eluant system is necessary, and analysis times are shortened ; secondly, solvents such as benzene and toluene do not interfere.

Finally, although the use of the electrochemical detection with reversed-phase chromatography system increases also the analysis selectivity, this method loses part of its relevance in view of the time-dependent decrease in the detector response, due to a "passivation" of the glassy carbone electrode.

The method is also convenient to analyse the 1-(2-pyridyl)piperazine isocyanate derivatives. However, an increase in the polarity of the mobile phase is required to shorten the elution time.

CONCLUSION

This normal-phase HPLC method can be performed by the analytical chemists for the determination of isocyanate concentration in air or in commercial polyurethane prepolymers, using piperazine reagents. It offers the advantage of restricting interference possibilities and being useful for the routine analysis of a large number of air samples or commercial polyurethane products, where the presence of isocyanate monomers and oligomers is suspected : nevertheless, isolation of oligomer-derivative standards is necessary.

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REFERENCES

[1] C.J. PURNELL and R.F. WALKER
Methods for the Determination of Atmospheric Organic Isocyanates. A Review.
Analyst, 110, 893-905, (1985)

[2] R.F. WALKER, P.A. ELLWOOD, H.L. HARDY and P.A. GOLDBERG
Separation of isocyanate prepolymer components as their urea derivatives by reversed-phase high-performance liquid chromatography.
J. Chromatogr., 301, 485-491, (1984)

[3] K. TAYMAZ
The analysis of toluene diisocyanate and diphenylmethane diisocyanate by gel-permeation chromatography.
J. Liq. Chromatogr., 9 (15), 3347-3356, (1986)

[4] L.A. PAPAZIAN
Characterisation of new isocyanate adducts by high performance size exclusion chromatrography.
J. Liq. Chromatogr., 9 (1), 67-68 , (1986)

[5] K.L. DUNLAP, R.L. SANDRIDGE and J. KELLER
Determination of Isocyanates in Working.
Atmospheres by High Speed Liquid Chromatography.
Anal. Chem., 48, 497-499 (1976)

[6] C. SANGÖ and E. ZIMERSON
A new reagent for determination of isocyanates in working atmospheres by HPLC using UV or fluorescence detection.
J. Liq. Chromatogr., 3 (7), 971-990 (1980)

[7] L.H. KORMOS, R.L. SANDRIDGE and J. KELLER
Determination of Isocyanates in Air by Liquid Chromatography with Fluorescence detection.
Anal. Chem., 53 , 1122-1129 (1981)

[8] C.J. WARWICK, D.A. BAGON and C. J. PURNELL
Application of Electrochemical Detection to the Measurement of Free Monomeric Aromatic and Aliphatic Isocyanates in Air by High-Performance Liquid Chromatography.
Analyst, 106, 676-685 (1981)

[9] P.A. GOLDBERG, R.F. WALKER, P.A. ELLWOOD and H.L. HARDY
Determination of trace atmospheric isocyanate concentrations by reversed-phase high-performance liquid chromatography using 1-(2-pyridyl)piperazine reagent.
J. Chromatogr., 212, 93-104 (1981)

[10] S.D. MEYER and D.E. TALLMAN
The determination of Toluene diisocyanate in Air by High Perfomance Liquid Chromatography with Electrochemical Detection.
Anal. Chimica Acta, 146, 227-236 (1983)

[11] D.A. BAGON, C.J. WARWICK and R.H. BROWN.
Evaluation of Total Isocyanate in Air Method Using 1-(2-Methoxyphenyl)piperazine and HPLC.
Am. Ind. Hyg. Assoc. J., 45(1), 39-43 (1984)

[12] A. ROBERT and P. SIMON
A Solvent-Free Sampling Method for Airborne Toluene Diisocyanate.
Chromatographia, 23 (7), 507-511 (1987)

[13] C. SANGÖ
Improved method for determination of traces of isocyanates in working atmospheres by high-performance liquid chromatography.
J. Liq. Chromatogr., 2 (6) 763-774 (1979)