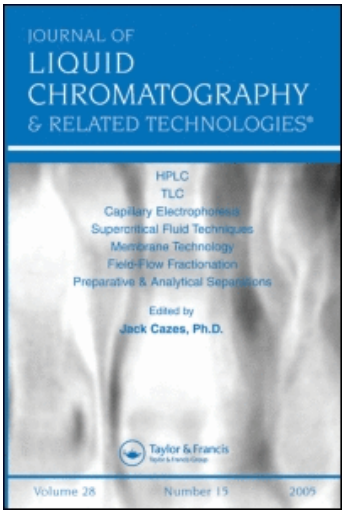

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Improved Method for Determination of Traces of Isocyanates in Working Atmospheres by High Performance Liquid Chromatography

C. Sangö[a]
[a] Technical Analytical Chemistry, Chemical Center, Lund, Sweden

To cite this Article Sangö, C.(1979) 'Improved Method for Determination of Traces of Isocyanates in Working Atmospheres by High Performance Liquid Chromatography', Journal of Liquid Chromatography & Related Technologies, 2: 6, 763 — 774
To link to this Article: DOI: 10.1080/01483917908060102
URL: http://dx.doi.org/10.1080/01483917908060102

JOURNAL OF LIQUID CHROMATOGRAPHY, 2(6), 763-774 (1979)

IMPROVED METHOD FOR DETERMINATION OF TRACES OF ISOCYANATES IN WORKING ATMOSPHERES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

C. Sangö
Technical Analytical Chemistry, Chemical Center
P.O.B. 740, S-220 07 Lund 7, Sweden

ABSTRACT

Isocyanates common in industrial environments were converted to urea derivatives by reaction with N-4-nitrobenzyl-N-*n*-propylamine. The urea derivatives were analyzed by high performance liquid chromatography on a bonded octadecylsilyl phase using isocratic elution with acetonitrile-water 75:25 v/v. The water phase contained 1% triethylamine and was adjusted to pH 3.0 with phosphoric acid. The method was applied to toluene 2,4- and 2,6-diisocyanate (2,4- and 2,6-TDI), hexamethylene diisocyanate (HDI), 4,4'-diphenylmethane diisocyanate (MDI) and Desmodur N 75 (DN 75). Comparison with previous liquid chromatographic methods shows that the elution time is about halved and the detection limits about five times lower in our case.

INTRODUCTION

Isocyanates are widely used in the manufacture of polyurethane foams, coatings and elastomers. Accordingly these substances occur in many industrial environments and because of the potential health hazards involved in their handling it is of vital interest to be able to assess their concentration in working atmospheres. For this purpose various methods have been developed.

The common methods for the determination of isocyanates in the environment have for a long time been the colorimetric method of Marcali (1), originally developed for toluene 2,4-diisocyanate, and its later modifications (2,3). These methods involve hydroly-

sis of the isocyanate to the corresponding aromatic amine, which is diazotised and coupled to form a coloured azo compound. Another colorimetric method is that of Pilz and Johann (4), in which the amine formed on hydrolysis is reacted with 1-fluoro-2,4-dinitrobenzene. This method has been applied to the determination of hexamethylene diisocyanate in air.

The colorimetric methods obviously have their limitations:

- low sensitivity; the detection limit for toluene diisocyanate is *e.g.* 0.03 mg/m^3 based on a 20 l air sample;
- interference from primary aromatic amines, and in the method of Pilz and Johann also from primary and secondary aliphatic and aromatic amines;
- the diazotation methods can only be applied to aromatic isocyanates;
- the methods are sensitive to minor changes in experimental conditions;
- if several isocyanates are in a mixture, only their sum is obtained, and the result is semiquantitative.

With the advent of the gas chromatographic method of Wheals and Thomson (5), it became possible to individually determine several isocyanates in a mixture quantitatively. However, the method was only utilized for the determination of toluene 2,4-diisocyanate and has so far not been tested on a broader scale.

Thin layer chromatography (6) also allow the determination of individual isocyanates in a mixture. The method is applicable to both aromatic and aliphatic isocyanates in air, but has several disadvantages:

- low sensitivity; the detection limit for toluene diisocyanate is 0.04 mg/m^3 based on a 20 l air sample;
- the results are at best semiquantitative;
- the separation is a rather tedious procedure.

A liquid chromatographic method which eliminates these limitations was recently described by Dunlap *et al.* (7). N-4-Nitrobenzyl-N-*n*-propylamine was used to convert the isocyanates to stable urea derivatives, which were separated on a pellicular silica column

using gradient elution. The method is applicable to both aromatic and aliphatic isocyanates at levels of interest in environmental industrial analysis. The detection limit for toluene diisocyanate is 0.005 mg/m^3, based on a 20 l air sample.

Hastings Vogt *et al.* (8,9) subsequently demonstrated the separation and quantitative determination of the same urea derivatives on different microparticulate silica packings. They pointed out that the excessive amount of reagent present in the solution of urea derivatives poses a problem. The reagent has a tendency to adhere to the silica, causing the urea derivatives to elute with a sloping background. This reduces the precision, especially for late peaks, and is also a serious threat to column life. It also follows that it takes a considerable time to restore the column to the original conditions after an analysis has been made. Another disadvantage with the existing liquid chromatographic methods is the necessity of using gradient elution, which complicates the procedure and makes the equipment more expensive.

It was felt that a more convenient liquid chromatographic method for isocyanate analysis in the form of urea derivatives could be developed by applying another type of column material and changing the eluent. Preliminary experiments indicated that reversed phase chromatography on a bonded octadecylsilyl ($C_{18}Si\equiv$) phase was the best choice, and that isocratic elution would be applicable.

EXPERIMENTAL

Apparatus

An Altex model 110 solvent metering pump was used together with a Rheodyne model 7105 (Rheodyne, Berkeley, Calif., U.S.A.) sampling valve injector with a 175 µl loop. The detector was an LDC model 1203 UV monitor, wavelength 254 nm, with an 8 µl cell (Laboratory Data Control, Riviera Beach, Fla., U.S.A.)

Column packing material and eluents

The packing material was Nucleosil 5 C_{18} (Macherey-Nagel & Co., Düren, G.F.R., art. 712 13). The mean particle diameter was 5 µm.

The eluents were methanol, acetonitrile or tetrahydrofuran with various water contents.

Column tubing and fittings

The columns consisted of 6.35 mm O.D. x 200 mm lengths of 316 stainless steel tubing with a polished inner surface. The internal diameter was 5 mm. They were equipped with Parker-Hannifin compression fittings. Very thin stainless steel mesh discs were placed at both ends of the column (part No. 206, hetp, 34 Gonville Avenue, Sutton, Macclesfield, Cheshire, England, SK 11 OEG). The valve injector and detector were connected to the column via 1/16" O.D. (0.15 mm I.D.) stainless steel tubing.

Column packing technique

Columns were packed according to the upward slurry packing technique (10). A Haskel pneumatic amplified pump model DST-150 (Haskel Engineering and Supply Co., Burbank, Calif. 91502, U.S.A.) was pressurized with acetone to 200 atm with a Whitey valve model NB-SS-3NBF4 (Whitey Company, Oakland, Calif., U.S.A.), closed on the outlet side. About 2.7 g of packing material was slurried in 70 ml chloroform in an ultrasonic bath for 10 minutes. The slurry reservoir Crawford type 304-HDF4-75 (part of a slurry packing kit, part No. 316, hetp, 34 Gonville Avenue, Sutton, Macclesfield, Cheshire, England, SK 11 OEG) was filled and the column mounted pointing upwards. Chloroform was filled to the top of the column. The end fitting was connected and the valve was opened. About 250 ml of solvent was passed, and the column was turned pointing downwards. The valve was closed, and after 5 minutes the column was disassembled, washed with metanol and tested.

Chemicals

Solvents. Acetonitrile, tetrahydrofuran and methanol were all high purity solvents for liquid chromatography (Rathburn Chemicals, Caberston Road, Walkersburn, Peeblesshire, Scotland, E H43 6AV).

Isocyanates. The hexamethylene diisocyanate (HDI), 4,4'-diphenylmethane diisocyanate (MDI) and Desmodur N 75 (DN 75) (a 75% w/w

solution of a high molecular weight biuret of HDI in 2-ethoxyethyl-acetate/xylene 1:1) were obtained from Bayer AG, Leverkusen, Germany.

The toluene diisocyanate was a mixture of 65% toluene 2,4-diisocyanate (2,4-TDI) and 35% toluene 2,6-diisocyanate (2,6-TDI) from E. Merck.

Reagent. The nitro-reagent (N-4-nitrobenzyl-N-*n*-propylamine) was prepared by the method of Dunlap *et al.* (7).

Procedure

A midget impinger is filled with 10 ml of the nitro reagent absorber solution (2×10^{-4} mol l^{-1} in toluene), and 15 l of air is drawn through the impinger at a rate of 1 l/min. After the sample is taken, the solution is evaporated to dryness at 35°C under vacuum. The residue is dissolved in 1 ml of the chromatographic eluent and 100 µl of the solution is injected into the chromatograph. The quantitative analysis was based on peak height measurement, and standard curves were prepared by chromatographing solutions of known composition.

RESULTS AND DISCUSSION

The presence of the basic reagent in the reaction mixture to be chromatographed poses certain problems when silica is used as column material. In fact, these problems could have been anticipated, as the difficulties of chromatographing basic compounds on silica are well known (11). The main cause is the presence of silanol groups on the silica surface which interact with and retard the reagent amine (12). A change to a reversed phase mode, using a C_{18} phase and aqueous solvents as eluents did not entirely avoid problems, since the reagent still eluted as a broad peak after the urea derivatives. This indicates that the silanol groups are not wholly removed from the silica surface during the preparation of the C_{18} phase. However, on addition of 1% triethylamine and adjusting the pH-value to 3.0 with phosphoric acid, the chromatographic picture dramatically changes. The reagent is now eluted with the

solvent front and no disturbance of the separation of the urea derivatives occurs. The main reason for this improvement is the protonization of the reagent amine, causing it to move rapidly through the column.

In order to be able to choose the best conditions for the chromatographic separation, a detailed study of the variation of k'-values for several urea derivatives with the composition of three common eluents was made, namely: methanol, acetonitrile and tetrahydrofuran (Figs. 1-3).

At low water content the urea derivatives elute fairly rapidly from the column, especially with aqueous tetrahydrofuran as eluent. On increasing the water content, the k'-values increase, reflecting the dominant influence of the nonpolar parts of the urea derivatives on retention. For all solvents, the MDI and DN 75 derivatives elute last in accordance with their high molecular weight. Retention of the HDI and 2,4- and 2,6-TDI derivatives is influenced by the kind of solvent and the water content. The increasing difference in retention between the structurally closely related 2,4- and 2,6-TDI derivatives in the solvent series methanol-acetonitrile-tetrahydrofuran is especially noteworthy. In a total analysis, the most difficult separation to achieve in a reasonable time is that between the 2,4- and 2,6-TDI derivatives and the HDI derivative.

Fortunately the separation problem is simplified, since the occurrence of all five isocyanates in the same working atmosphere is rather unlikely. Thus, 2,4- and 2,6-TDI and MDI are used for the preparation of foam and rubber, while DN 75 containing about 1% of HDI mainly occurs in the paint and lacquer industry. On that account we have merely tried to develop methods for separating the isocyanates within the two groups isocratically in the shortest possible time.

On the basis of the k'-curves in Figs. 1-3, aqueous acetonitrile containing 25% v/v water was chosen. Other solvent compositions, *e.g.* aqueous methanol, give comparable, although not quite as good, separations. Another advantage with acetonitrile is the low pressure needed to get an acceptable solvent flow through the column.

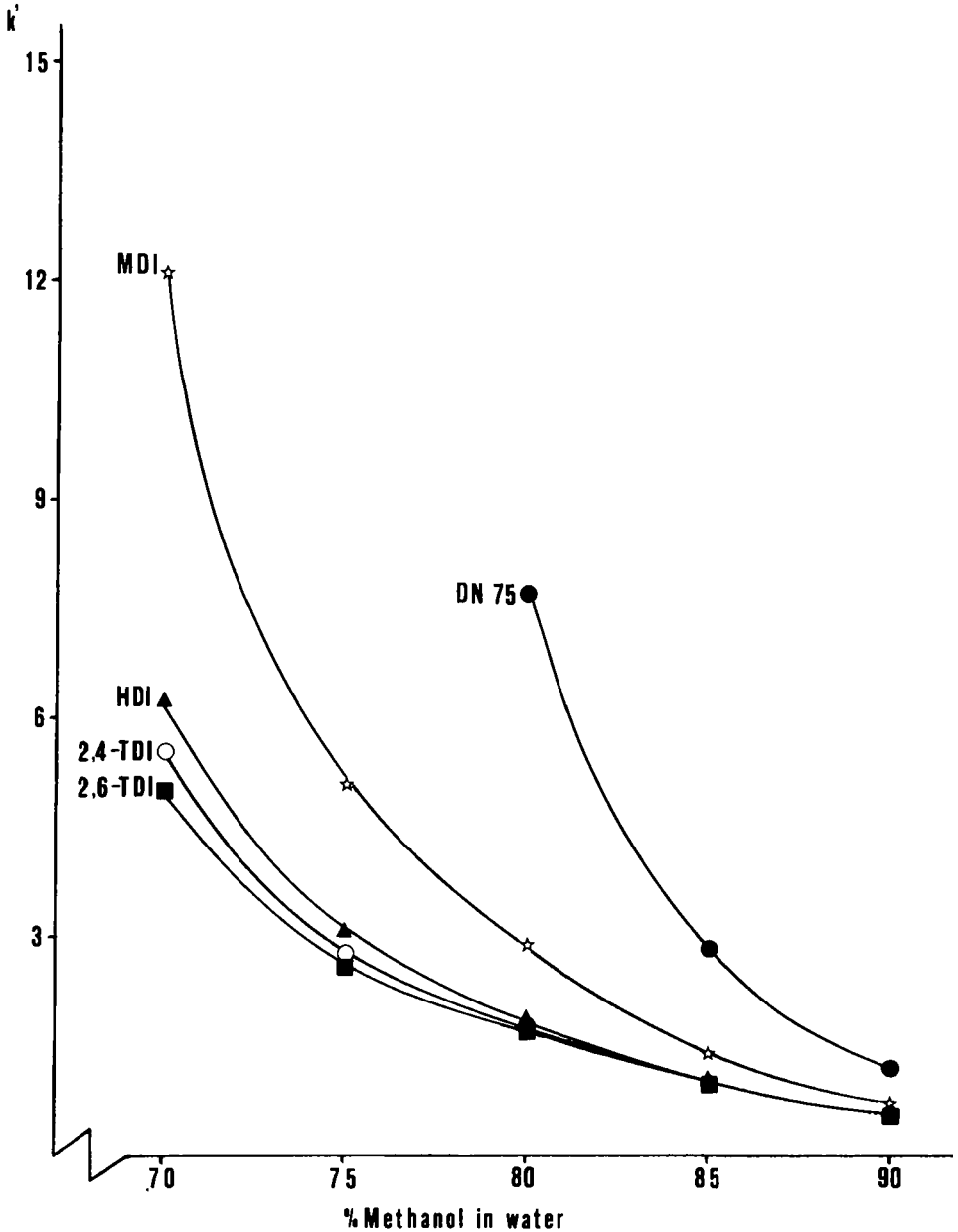

FIGURE 1

Relationship between capacity factor, k', for urea derivatives and methanol content of the mobile phase. Column: Nucleosil 5 C_{18}. Eluent: methanol-water, the water phase containing 1% triethylamine and adjusted to pH 3.0 with phosphoric acid. Flow rate: 1 ml min^{-1}.

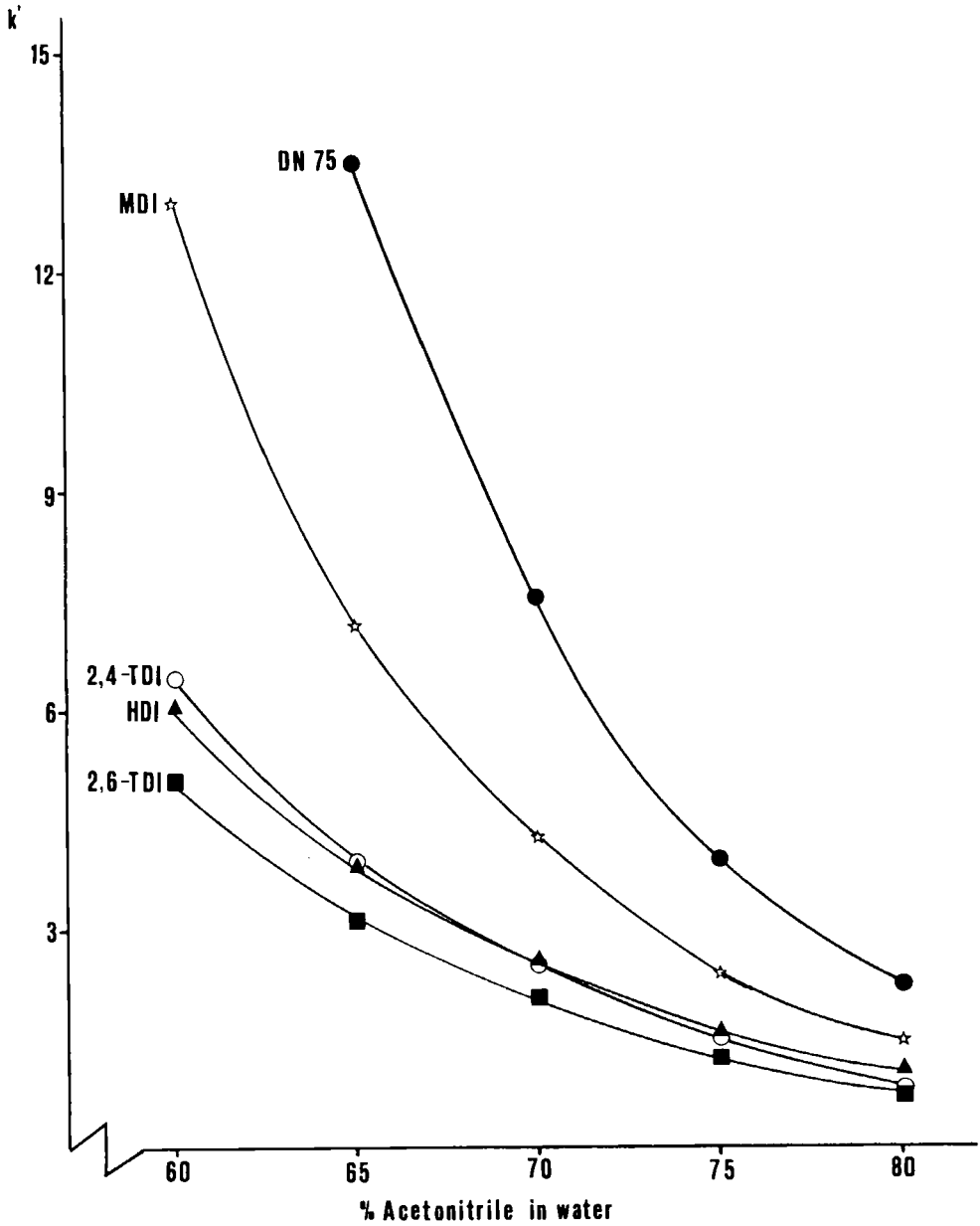

FIGURE 2

Relationship between capacity factor, k', for urea derivatives and acetonitrile content of the mobile phase. Column: Nucleosil 5 C_{18}. Eluent: acetonitrile-water, the water phase containing 1% triethylamine and adjusted to pH 3.0 with phosphoric acid. Flow rate: 1 ml min^{-1}.

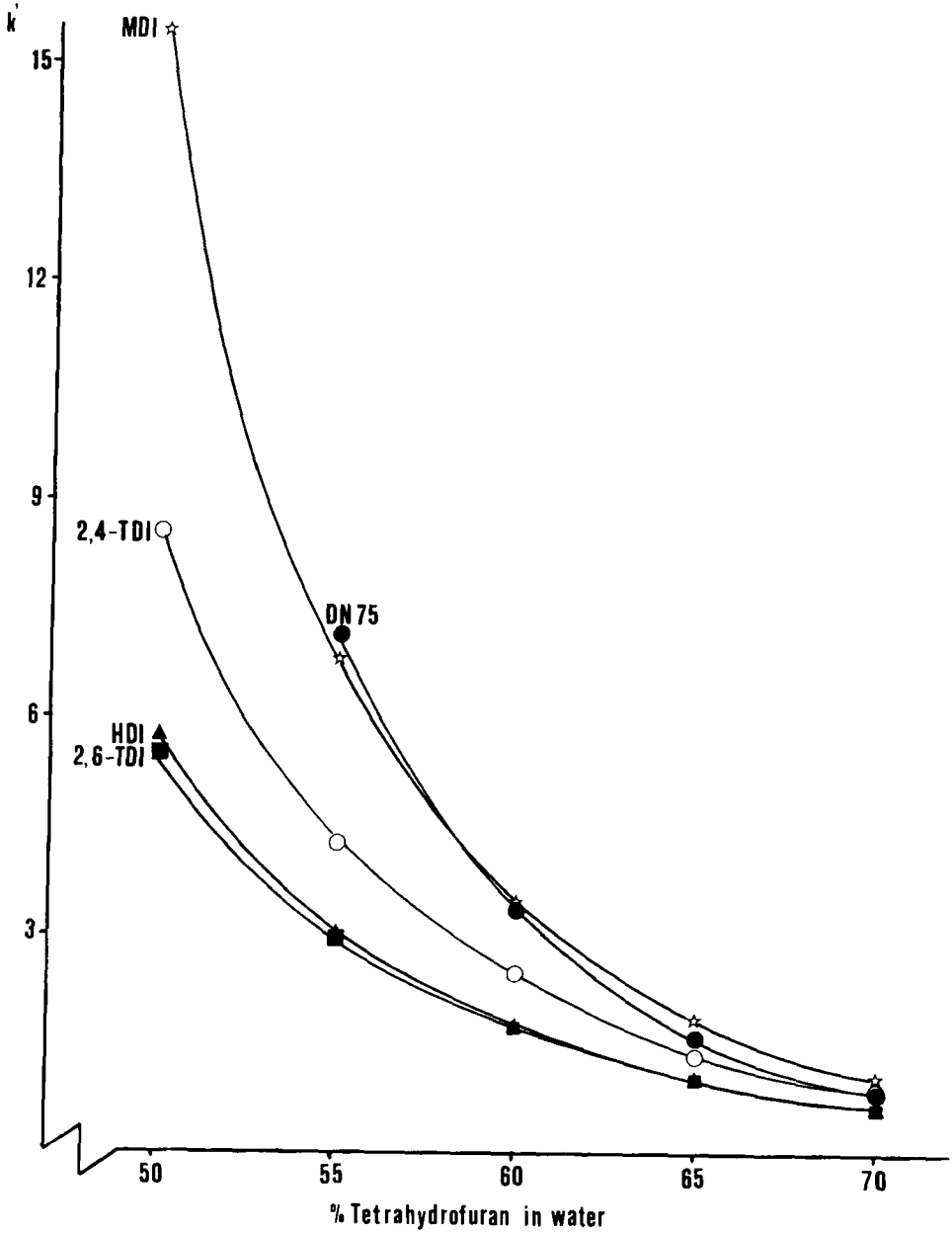

FIGURE 3

Relationship between capacity factor, k', for urea derivatives and tetrahydrofuran content of the mobile phase. Column: Nucleosil 5 C_{18}. Eluent: tetrahydrofuran-water, the water phase containing 1% triethylamine and adjusted to pH 3.0 with phosphoric acid. Flow rate: 1 ml min^{-1}.

As shown by Fig. 4 the separation of a mixture of 2,4- and 2,6-TDI and MDI is complete in five minutes, and since the elution mode is isocratic, the column is immediately ready for a new injection. The analysis of a mixture of HDI and DN 75 takes about seven minutes. Detection limits of the method are given in Table I.

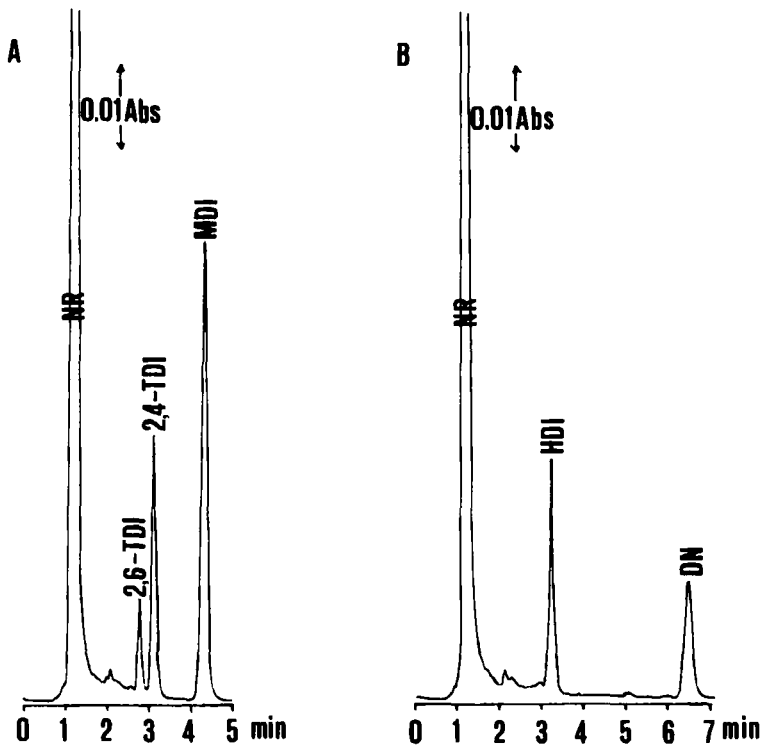

FIGURE 4

Chromatogram of nitro reagent and urea derivatives. Eluent: acetonitrile-water 75:25 v/v, the water phase containing 1% triethylamine and adjusted to pH 3.0 with phosphoric acid. Flow rate: 2 ml min^{-1}. Sample volume: 100 µl. Detector: UV at 254 nm and 0.128 AUFS.

a) Determination of 2,6-TDI, 2,4-TDI and MDI. Isocyanate concentrations: 0.35 µg 2,6-TDI/ml, 0.65 µg 2,4-TDI/ml and 1.0 µg MDI/ml.

b) Determination of HDI and DN 75. Isocyanate concentrations: 1.2 µg HDI/ml and 6.0 µg DN 75/ml.

TABLE I

Detection limits for several isocyanates

Isocyanate	Detection limit mg/m^3
2,4-TDI	0.001
2,6-TDI	0.001
HDI	0.002
MDI	0.001
Desmodur N 75	0.015

*The detection limits are based on a 1[illegible] air sample and the experimental conditions as in Fig. 4.

Comparison with the method of Dunlap *et al.* (7) utilizing a silica phase and gradient elution shows that the elution time is about halved in our case and that the two TDI derivatives are fully separated. Furthermore, our detection limits are about five times lower than those of Dunlap *et al.* The C_{18} column has turned out to be very stable: hundreds of samples have been run with no noticable change of the column performance. It thus appears that the present method has a number of advantages which should make it useful for the analytical chemist working with isocyanates.

ACKNOWLEDGMENT

This investigation was supported by a grant from the Swedish Work Environment Fund.

REFERENCES

1. Marcali, K., Anal. Chem. 29, 552 (1957).

2. Grim, K.E. and Linch, A.L., Amer. Ind. Hyg. Ass. J. 25, 285 (1964).

3. Meddle, D.W., Radford, D.W. and Wood, R., Analyst 94, 369 (1969).

4. Pilz, W. and Johann, I., Mikrochim. Acta 351 (1970).

5. Wheals, B.B. and Thomson, J., Chem. & Ind. (London) 753 (1967).

6. Keller, J., Dunlap, K.L. and Sandridge, R.L., Anal. Chem. 46, 1845 (1974).

7. Dunlap, K.L., Sandridge, R.L. and Keller, J., Anal. Chem. 48, 497 (1976).

8. Hastings Vogt, C.R., Ko, C.Y. and Ryan, T.R., J. Chromatogr. 134, 451 (1977).

9. Hastings Vogt, C.R., Ko, C.Y. and Ryan, T.R., U.S. NTIS, PB Rep. 1976, BP-262675.

10. Bristow, P.A., Brittain, P.N., Riley, C.M., and Williamson, B.F., J. Chromatogr. 131, 57 (1977).

11. Jane, J., J. Chromatogr. 111, 227 (1975).

12. Karger, B.L. and Giese, R.W., Anal. Chem. 50, 1048A (1978).