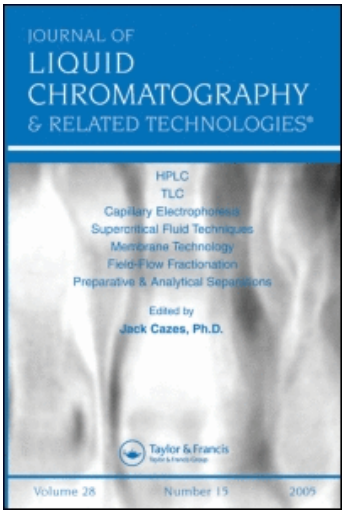

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A NEW REAGENT FOR DETERMINATION OF ISOCYANATES IN WORKING ATMOSPHERES BY HPLC USING UV OR FLUORESCENCE DETECTION

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ABSTRACT

A new liquid chromatographic method with increased sensitivity has been developed for the determination of isocyanates common in industrial environments. The isocyanates are converted to stable urea derivatives by reaction with 9-(N-methylaminomethyl)-anthracene. These derivatives were analyzed using high performance liquid chromatography on a bonded octadecylsilyl phase using isocratic elution with acetonitrile/water and detected either by a UV or a fluorescence detector. The method was applied to toluene 2,4- and 2,6-diisocyanate (2,4- and 2,6-TDI), hexamethylene diisocyanate (HDI) and 4,4'-diphenylmethane diisocyanate (MDI).

The influence of various salts on the retention of the reagent amine was studied, as well as the separation of the urea derivatives on different C_{18}-phases. The detection limit is about $1 \cdot 10^{-4}$ mg/m^3 for the isocyanates investigated, using either UV or fluorescence detection. This means that the new method is ten to twenty times more sensitive than the previously described reversed phase LC method, which utilized N-4-nitrobenzyl-N-*n*-propylamine as reagent.

INTRODUCTION

In a recent paper by one of the present authors, an improved method for the determination of traces of isocyanates in working atmospheres by high performance liquid chromatography (HPLC) was described (1). This method utilized the reaction between isocyanates and N-4-nitrobenzyl-N-*n*-propylamine to form urea derivatives, which were separated by HPLC and monitored by an UV detector at

254 nm. It was demonstrated that by applying reversed phase chromatography on a bonded octadecylsilyl phase, instead of adsorption chromatography on silica as previously used (2,3), separation between the reagent and the urea derivatives was improved, the analysis time was shortened, and the procedure simplified, since isocratic elution could be used instead of gradient elution.

In the present investigation, a new amine reagent for converting isocyanates to ureas for further separation by HPLC is introduced. The new reagent is 9-(N-methylaminomethyl)-anthracene, the urea derivatives of which exhibit fluorescence in addition to having a very strong UV-absorption (molar absorptivity $\approx 4 \times 10^5$ l $mol^{-1}cm^{-1}$ at 254 nm). It is thus possible to monitor the eluate from the HPLC separation by using either a UV or a fluorescence detector.

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 UV detector was an LDC model 1203 UV monitor, wavelength 254 nm, with a 10 µl cell (Laboratory Data Control, Riviera Beach, Fla., U.S.A.). The fluorescence detector was a MPF-2A fluorescence spectrophotometer with a 40 µl cell (Perkin Elmer, Norwalk, Connecticut, U.S.A.).

Column packing material and packing technique

Six different commercially available C_{18}-packing materials were used. The mean particle diameter was 5 or 10 µm: ODS-Hypersil (5 µm, Shandon Southern Products Limited, Gt. Britain). LiChrosorb RP 18 (10 µm, E. Merck, Darmstadt, G.F.R.), µBondapak C_{18} (10 µm, Waters Associates Inc., Milford, Massachusetts, U.S.A.), Nucleosil C_{18} (5 µm, Macherey-Nagel & Co., Düren, G.F.R.), Partisil ODS (10 µm, Whatman Inc., 9 Bridewell Place, Clifton, New Jersey, U.S.A.), Spherisorb ODS (5 µm, Phase Separation Ltd., Deeside Industrial Estate, Queensferry, Clwyd, Gt. Britain).

The columns consisted of 6.35 mm O.D. × 200 mm lengths of 316 stainless steel tubing with a polished inner surface. The internal diameter was 5 mm.

The column packing technique has been described elsewhere (1).

Chromatographic eluent

The eluent consisted of a mixture of acetonitrile and water. The water phase contained either organic (triethylammonium phosphate, diethylammonium phosphate, n-butylammonium phosphate) or inorganic salts (sodium phosphate, sodium sulphate, sodium nitrate, ammonium nitrate). The pH of the aqueous phase was adjusted to 3.0 with phosphoric acid.

The capacity factors (k') were calculated as the mean from at least two injections. The column void volume was estimated by the injection of sodium nitrate when the UV-detector was used.

Chemicals

Solvents. Acetonitrile: pro analysi grade (E. Merck). Water: doubly distilled. Other solvents used (dimethylformamide, toluene and methylene chloride) were all of pro analysi quality (E. Merck). Toluene and methylene chloride were further dried.

Isocyanates. Hexamethylene diisocyanate (HDI) and 4,4'-diphenylmethane diisocyanate (MDI) were obtained from Bayer AG, Leverkusen, G.F.R. The toluene diisocyanate was a mixture of 65% w/w toluene 2,4-diisocyanate (2,4-TDI) and 35% toluene 2,6-diisocyanate (2,6-TDI) from E. Merck.

Other chemicals. Triethylamine, diethylamine and *n*-butylamine were obtained from E. Merck.

Reagent. The reagent, 9-(N-methylaminomethyl)-anthracene was prepared in the following way. Methylamine (5 g, 160 mmol, 33% water solution) was slowly added to a solution of 9-anthracenealdehyde (11.2 g, 53 mmol) in ethanol (500 ml). The reaction mixture was heated under reflux (0.5 h), cooled and hydrogenated (atm. pressure) with Rainey nickel (6 g) as catalyst. After the completion of the reduction (12 - 24 h) the catalyst was removed by filtration and

the ethanol was evaporated under reduced pressure (50°C). The residue was dissolved in acetone (200 ml) and the salt of the product was formed by the addition of conc. hydrochloric acid (4.5 ml). The salt was removed by filtration and recrystallized from ethanol (200 ml). The product is stored as the hydrochloride because of its greater stability. A solution of the salt (1.5 g) in water (300 ml) was made alkaline with NaOH and extracted with toluene. The toluene layer was evaporated under reduced pressure (50°C) to give the product. (M.p., 57.5°-58°C, NMR ($CDCl_3$)δ 1.45 (S, 1H, -NH), 2.64 (S, 3H, $-CH_3$), 4.66 (S, 2H, $-CH_2-$) 7.4-8.4 (9H, aromatic) ppm; CHN analysis, calculated for $C_{16}H_{15}N$: C 86.83, H 6.83, N 6.33; found, C 86.46, H 6.87, N 6.26.

Preparation of urea derivatives from 9-(N-methylaminomethyl)-anthracene and diisocyanates. The reaction was carried out at 25°C under nitrogen. The diisocyanate (2.0 mmol) was dissolved in dry methylene chloride (25 ml) and the solution was slowly added to a solution of 9-(N-methylaminomethyl)-anthracene (1.3 g, 6.0 mmol) in methylene chloride (50 ml). The reaction mixture was stirred (1.5 h) and concentrated until the appearance of the solid products, cooled with ice and the products formed removed by filtration. The HDI derivative was recrystallized from methylene chloride and the derivatives from TDI and MDI by continuous extraction.

The ureas obtained are very difficult to dissolve in most solvents, except dimethylformamide.

Preparation of reagent absorber solution. For stability, the 9-(N-methylaminomethyl)-anthracene reagent is stored as its hydrochloride. Dissolve about 25 mg of the reagent hydrochloride in 5 ml of 0.1 mol l^{-1} HCl. Extract the reagent solution twice with 5 ml of toluene and discard the toluene. Add 5 ml of 1.0 mol l^{-1} NaOH, whereupon the free amine precipitates. Extract the free amine with 5 ml of toluene. Dilute the resulting solution to 100 ml with toluene to prepare the 1×10^{-3} mol l^{-1} solution. Dilute this solution tenfold with toluene to obtain the 1×10^{-4} mol l^{-1} solution which is used as the reagent solution. If stored in darkness in a refrigerator, the

reagent solution is stable for several months. However, a certain decomposition of the reagent may take place; it is therefore recommended to run a chromatogram of the reagent solution before use.

Preparation of standard solutions. Standard solutions of the urea derivatives were made up as follows. On account of the low solubility of the urea derivatives in the eluent a stock solution was prepared in dimethylformamide. About 25 mg was exactly weighed out and dissolved in 50 ml dimethylformamide. This solution, when kept in darkness in a refrigerator, can be stored for at least 6 months.

To prepare a solution suitable for injection, an aliquot is withdrawn from the stock solution and mixed with the eluent. The solution is then ready for injection into the chromatograph.

A simpler method obviating the synthesis of pure urea derivatives is the following. A stock solution is prepared from the pure isocyanate and the urea derivative formed *in situ* by mixing an aliquot of this solution with the reagent solution. About 10 mg of the pure isocyanate is exactly weighed out and dissolved in 50 ml of dry methylene chloride. An aliquot of the solution is added to 10 ml of the reagent solution and the mixture treated as described below for the air sample. The same results were obtained using the *in situ* method as with pure urea derivatives.

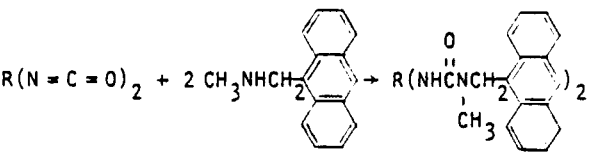
Air sampling procedure

A midget impinger is filled with 10 ml of the reagent absorber solution (1×10^{-4} mol l^{-1} in toluene), and 15 l of air is drawn through the impinger at a rate of 1 l min^{-1}. The collection efficiency is shown to be more than 95% for the isocyanates investigated with a flow rate between 0.5 and 2 l min^{-1}. 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 eluent and 1-150 µl of the solution is injected into the chromatograph. If the sample is not completely dissolved, which may occur for high isocyanate concentrations (*e.g.* more than 10 µg MDI derivative/ml eluent), 1 ml of dimethylformamide should be added. The injection volume should in

this case be reduced to 1-20 µl. The quantitative analysis was based on peak height measurement, and standard curves were prepared by chromatographing standard solutions of known composition.

RESULTS AND DISCUSSION

The determination of isocyanates with the 9-(N-methylaminomethyl)-anthracene reagent (MAMA) is based on the following reaction



In the previous work (1) which utilized N-4-nitrobenzyl-N-*n*-propylamine for the derivatization, the separation between the excess reagent and the urea derivatives was carried out on a bonded octadecylsilyl phase (Nucleosil 5 C_{18}) using isocratic elution with acetonitrile-water 75:25 v/v. The aqueous phase contained 1% v/v triethylamine and was adjusted to pH 3.0 with phosphoric acid.

In the absence of triethylammonium phosphate, the excess amine reagent exhibited a high affinity for the C_{18} phase ($k' > 30$). The behaviour of the present amine reagent and the urea derivatives studied in this work on C_{18} phases is, as expected, similar. Since it is essential for the analysis to get a clean separation between the excess reagent and the urea derivatives, the k' value of the reagent should be low, *i.e.* less than 1.0. The effects of different concentrations of triethylammonium phosphate and some other salts were therefore studied in some detail.

Effect of added salt on the elution of the amine reagent

The effect of triethylammonium phosphate (TEAP) concentration on the retention of the amine reagent is demonstrated in Table I for various commercial C_{18} phases.

TABLE I

Effect of triethylammonium phosphate (TEAP) concentration on the capacity factor, k', of the amine reagent, 9-(N-methylaminomethyl)-anthracene

C_{18} phase	0.1% TEA k'	0.5% TEA k'	1.0% TEA k'	5.0% TEA k'
ODS-Hypersil	3.2	0.48	0.43	0.08
LiChrosorb RP 18	2.9	0.50	0.38	0.12
µBondapak C_{18}	1.4	0.41	0.36	0.25
Nucleosil C_{18}	1.2	0.27	0.23	0.09
Partisil ODS	3.0	1.1	1.0	0.99
Spherisorb ODS	5.0	0.76	0.56	0.15

Eluent: Acetonitrile-water 80:20 v/v, the water phase containing 0.1 - 5.0% v/v triethylamine (TEA) and adjusted to pH 3.0 with phosphoric acid. Flow rate: 2 ml min^{-1}.

On increasing the concentration of TEAP, the k'-values of the reagent decrease rapidly up to a concentration of 0.5% and thereafter more gradually. The fact that the retention decreases on increasing the ionic strength of the eluent is in accordance with the results of Sugden et al. (4). It is also seen that the six commercial C_{18} phases tested differ in their behaviour. It is reasonable to assume that these values reflect differences in the properties of the silica matrix and in the methods of fixing the octadecylsilyl group to the matrix.

The kind of chlorosilane used, *e.g.* octadecyltrichlorosilane or an octadecylsilane in which one or two of the chlorine atoms have been exchanged for methyl groups, could also influence the properties of the phase, especially the number of remaining silanol groups, which are known to contribute to the chromatographic retention (5).

In addition to TEA the effects of some other organic bases, *i.e.* diethylamine and *n*-butylamine on the k'-value of the reagent amine were studied. Their influence was found to be similar to that of TEA. The maximum solubility of diethylammonium phosphate in acetonitrile-water 80:20 v/v is 2-3%. However, it turned out that the kind of base used also had a certain influence on the k'-values of the urea derivatives and the base can thus be used to govern their separation.

The effect of a number of inorganic salts *i.e.* sodium phosphate, sodium sulphate and sodium and ammonium nitrate were also studied. In all cases the pH was adjusted to 3.0 using phosphoric acid. As for the organic bases the k'-value of the reagent decreased as the concentration of salt increased. However, certain aqueous acetonitrile salt solutions cannot be made concentrated enough to prevent interference between reagent and urea derivatives. This is the case for sodium phosphate and sodium sulphate, while sodium and ammonium nitrate are usable. A disadvantage with the nitrate salts is, however, their high UV-absorbance at 254 nm.

Separation of the urea derivatives on different C_{18}-phases

Organic salts such as TEAP are apparently best suited to reduce the retention of the reagent amine. In order to get a rapid elution, a fairly high content of TEA in the aqueous phase (3% v/v) was chosen.

The variation of the capacity factor, k', for four urea derivatives, namely those of 2,6-TDI, 2,4-TDI, HDI and MDI, with the content of acetonitrile in the eluent for three different commercially available C_{18}-phases is demonstrated in Fig. 1. Chromatograms from the separation of urea derivatives of 2,6-TDI, 2,4-TDI, HDI and MDI are shown in Fig. 2.

There is a considerable variation in separation pattern with the kind of C_{18}-phase used. The reason for this was previously discussed in this paper. Different batches of the same phase can also differ in their chromatographic performance. However, these differences are generally less than those obtained for different makes of C_{18}-phase.

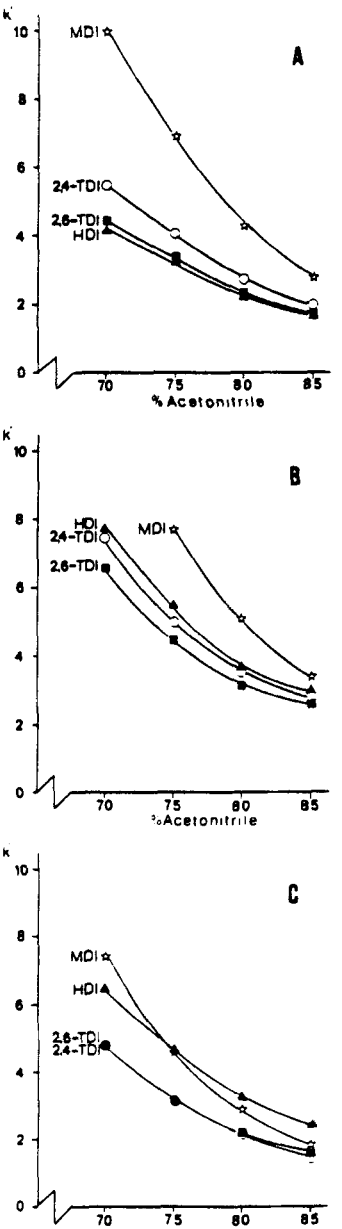


FIGURE 1

Relationship between capacity factor, k', for urea derivatives and acetonitrile content of the mobile phase. Eluent: acetonitrile-water, the water phase containing 3% v/v triethylamine and adjusted to pH 3.0 with phosphoric acid. Flow rate: 2 ml min^{-1}. Columns (5 x 200 mm): ODS-Hypersil (A), Nucleosil C_{18} (B) and Spherisorb ODS (C).

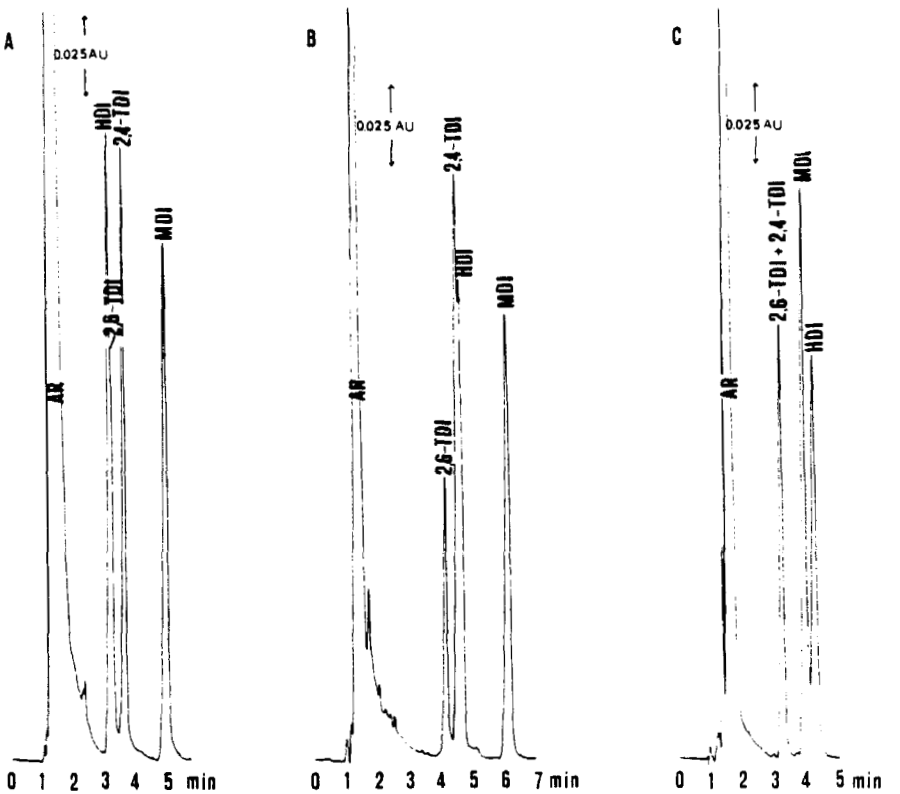


FIGURE 2

Chromatograms of 9-(N-methylaminomethyl)-anthracene reagent and urea derivatives. Eluent: acetonitrile-water 80:20 v/v, the water phase containing 3% v/v triethylamine (pH 3.0). Flow rate: 2 ml min^{-1}. Sample volume: 50 µl. Detector: UV at 254 nm and 0.256 AUFS. Isocyanate concentrations: 1.0 µg TDI (35/65)/10 ml reagent absorber solution (A,B), 0.5 µg TDI (35/65)/10 ml (C), 0.5 µg HDI/10 ml and 1.0 µg MDI/10 ml. Columns (5 × 200 mm): ODS-Hypersil (A), Nucleosil C_{18} (B) and Spherisorb ODS (C).

On all phases, a clean separation was achieved between the reagent amine and the ureas. No phase gave complete separation of all the urea derivatives. However, the occurrence of all four derivatives in the same working atmosphere is unlikely. It is, however, possible to run a mixture twice using two different pha-

ses, *e.g.* first on the Hypersil column and then on the Spherisorb column. Another possibility is to use other organic bases than TEA (see Fig. 3).

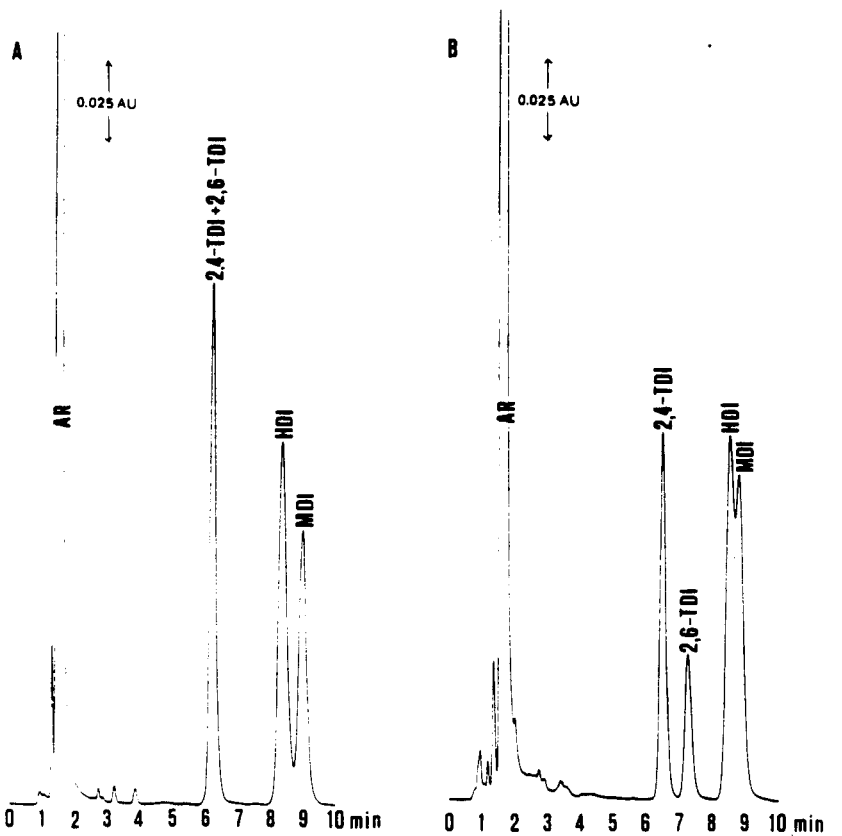


FIGURE 3

Chromatograms of 9-(N-methylaminomethyl)-anthracene reagent and urea derivatives. Flow rate: 2 ml min^{-1}. Sample volume: 50 µl. Detector: UV at 254 nm and 0.256 AUFS. Isocyanate concentrations: 1.0 µg TDI (35/65)/10 ml reagent absorber solution, 1.0 µg HDI/10 ml and 1.0 µg MDI/10 ml. Column (5 × 200 mm): Spherisorb ODS. Eluent: acetonitrile-water 70:30 v/v, the water phase containing 3% triethylamine, pH 3.0 (A) and 3% diethylamine, pH 3.0 (B).

Quantitative analysis

The quantitative analysis is based on peak height measurements, since there is a linear relationship between peak height and concentration of the urea derivatives, as shown in Fig. 4 for the HDI derivative.

At high concentrations of isocyanates, precipitation of urea derivatives can take place when the sample, after evaporation to dryness, is dissolved in the eluent, since the solubility of the ureas in the eluent is rather low. The solubility decreases in the order HDI > 2,4-TDI > 2,6-TDI > MDI. Thus, it is possible to dissolve more than 100 µg of the HDI urea per ml eluent [acetonitrile-water 80:20, 3% TEA (pH 3)], but only about 10 µg of the MDI urea. This difficulty can be circumvented by dissolving

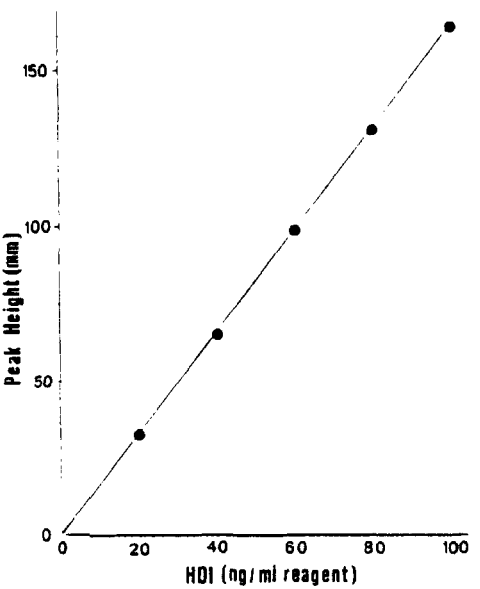


FIGURE 4

Relationship between peak height and the concentration of HDI urea derivative. Isocyanate concentrations: 0 - 1.0 µg/10 ml reagent absorber solution. Chromatographic conditions as in Fig. 2 B.

the ureas in pure dimethylformamide (DMF) or in a mixture of equal volumes of DMF and eluent. However, only about 20 µl of the DMF solutions can be injected without distortion of the peaks, compared to as much as 200-300 µl of the eluent solution.

Detection limit

The detection limit of the new method, using UV-detection at 254 nm, is of the order of $1 \cdot 10^{-4}$ mg/m^3 for the isocyanates investigated (TDI, MDI and HDI). The detection limit is based on a 15 l air sample and 100 µl injection volume. Comparison with the previous method, utilizing N-4-nitrobenzyl-N-*n*-propylamine, shows a ten to twentyfold improvement of the detection limit.

Stability of reagent and urea derivatives

A certain decomposition of the amine reagent (MAMA), as well as of N-4-nitrobenzyl-N-*n*-propylamine, takes place under the influence of light. This is demonstrated in Fig. 5 which shows chromatograms of a newly-made MAMA reagent solution and of a solution which has been exposed to sunlight for a couple of hours.

The decomposition products are eluted before the ureas. Accordingly, the risk of interference seems to be slight. The number and amount of decomposition products increase with time and temperature. The reagent solution should therefore be stored in darkness, and preferably in a refrigerator. The nature of the working atmosphere can also influence the appearance of extraneous peaks in the chromatogram. Thus, if the working atmosphere is oxidizing, the reagent decomposition can accelerate and secondary peaks can also arise if other amine-reactive substances than isocyanates, *e.g.* acid chlorides or acid anhydrides, are present. Furthermore, other kinds of isocyanate-reactive substances, *e.g.* alcohols, phenols, water, and amines can interfere with the analysis. However, preliminary experiments made at this laboratory indicate that due to the difference in reactivity with isocyanate between amines on one hand and alcohols, phenols and water on the other, only prim. and sec. aliphatic amines could possibly interfere.

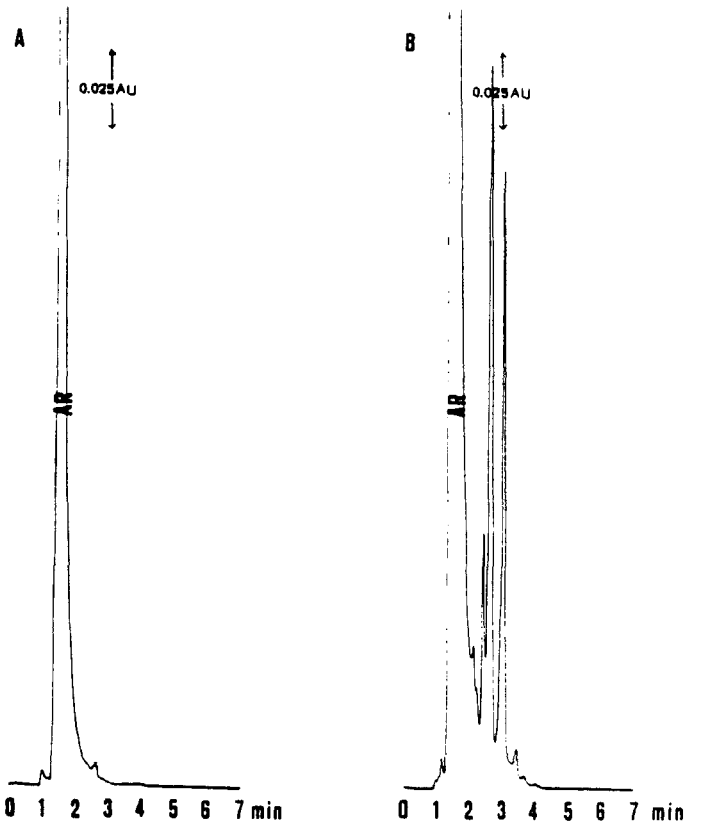


FIGURE 5

Chromatograms of 9-(N-methylaminomethyl)-anthracene reagent. Chromatographic conditions as in Fig. 2 B.
(A) Reagent absorber solution, stored in darkness.
(B) Reagent absorber solution, exposed to sunlight.

The occurrence of compounds absorbing at 254 nm in the working atmosphere, *e.g.* aromatic solvents, can also cause interference if the compounds in question have retentions similar to the ureas. However, the risk is slight since most volatile solvents are removed on the evaporation of toluene from the absorber solution.

The stability of the sample solution not only refers to the excess reagent, but also to the urea derivatives formed on reaction

of the isocyanates with the reagent. Fig. 6 illustrates the resistance to decomposition of the MDI-urea. Samples were stored in 10 ml of reagent absorber solution under varying conditions of light and temperature. It was found that when stored in darkness, the samples were insensitive to temperature change in the range 5-25°C, while a gradual decomposition took place in daylight. Similar results were obtained for the other ureas studied in this paper. These results are in agreement with those obtained for the reagent amine and indicate that samples should be kept in darkness until analysis takes place.

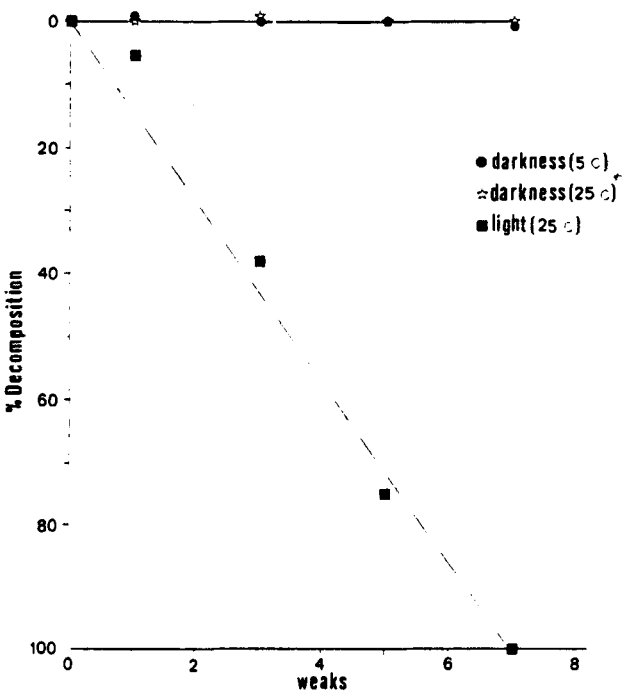


FIGURE 6

Relationship between decomposition of MDI urea derivative and time in darkness and light.
Isocyanate concentration: 1.0 µg MDI/10 ml reagent absorber solution.

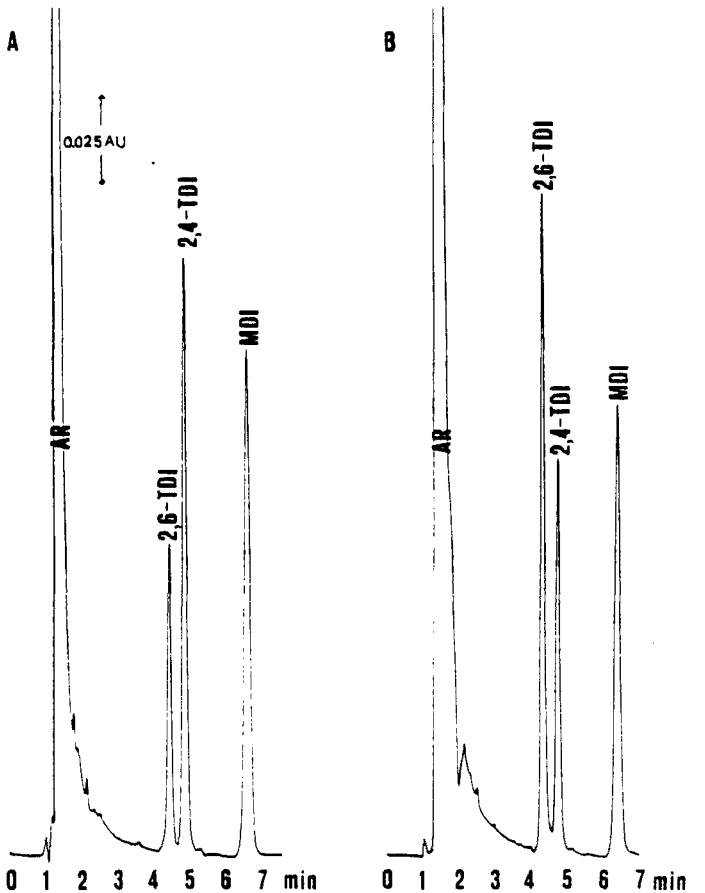


FIGURE 7

Chromatograms of 9-(N-methylaminomethyl)-anthracene reagent and urea derivatives. Isocyanate concentrations: 1.0 µg TDI (35/65)/10 ml reagent absorber solution and 1.0 µg MDI/10 ml. Column (5 × 200 mm): Nucleosil C_{18}. Chromatographic conditions as in Fig. 2 B. Detection:
(A) UV at 254 nm and 0.256 AUFS.
(B) Fluorescence, excitation (254 nm) and emission (412 nm).

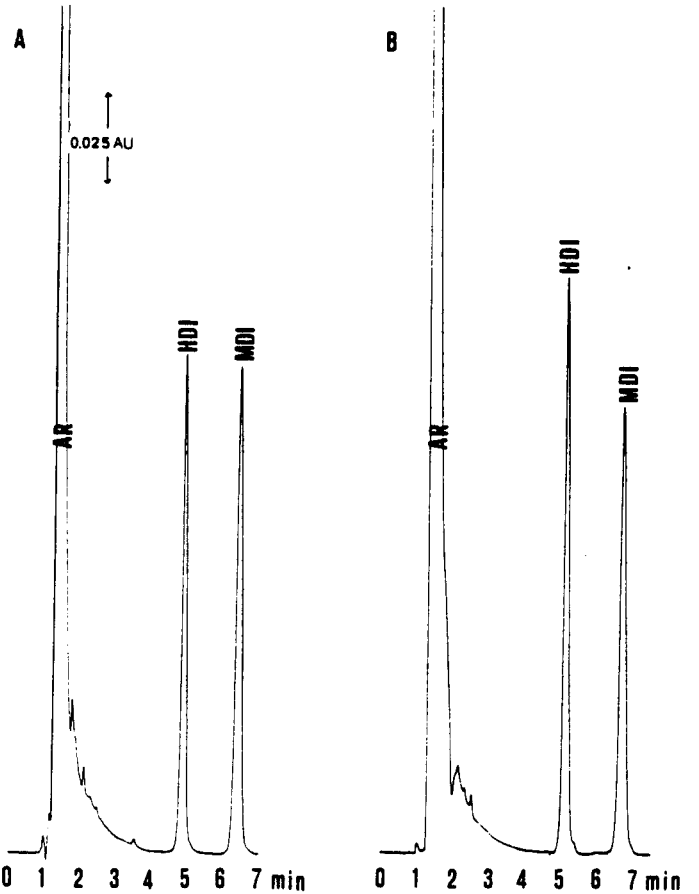


FIGURE 8

Chromatograms of 9-(N-methylaminomethyl)-anthracene reagent and urea derivatives. Isocyanate concentrations: 0.5 µg HDI/10 ml reagent absorber solution and 1.0 µg MDI/10 ml. Column (5 × 200 mm): Nucleosil C_{18}. Chromatographic conditions as in Fig. 2 B. Detection:
(A) UV at 254 nm and 0.256 AUFS.
(B) Fluorescence, excitation (254 nm) and emission (412 nm).

Fluorescence detection

The ureas formed on reaction between 9-(N-methylaminomethyl)-anthracene and isocyanates can also be assayed using fluorescence detection. In Figs. 7 and 8 the chromatograms obtained for two mixtures of urea derivatives, using either a UV- or a fluorescence detector, are presented. The attainable detection limits on fluorescence detection depend on the sensitivity of the detector used. In the pre-

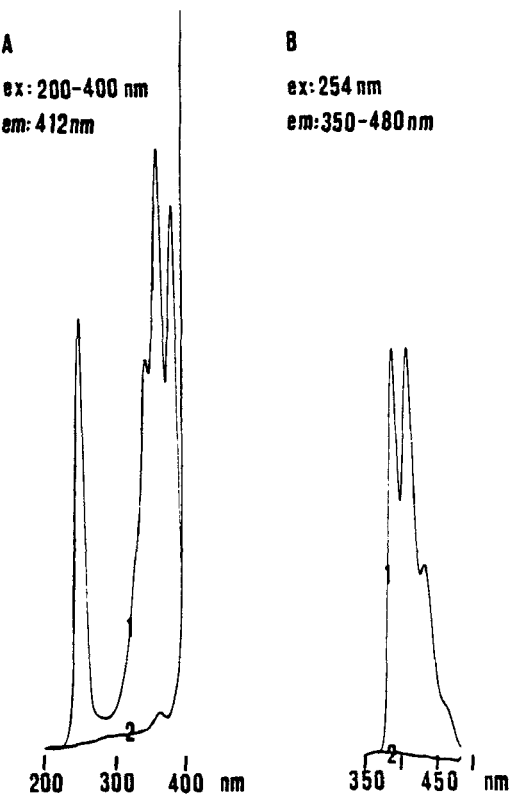


FIGURE 9

Emission spectrum (B) and excitation spectrum (A) of the HDI urea derivative. The spectra were obtained using 'stopped-flow' conditions. Chromatographic conditions as in Fig. 2 B. Spectrum of HDI derivative, corresponding to 0.5 µg HDI/10 ml reagent absorber solution (1). Spectrum of background (2).

sent case, where a Perkin-Elmer MPF-2 A detector was employed, the detection limits for TDI, MDI and HDI are about the same as for UV-detection at 254 nm, *i.e.* about $1 \cdot 10^{-4}$ mg/m^3.

However, the different sensitivities for 2,6- and 2,4-TDI, using the two detection modes, is noteworthy. A comparison between the UV- and fluorescence chromatograms shows that the resolution is somewhat better when UV-detection is used due to the fact that the UV-detector had a cell volume of 10 µl while that of the fluorescence detector was 40 µl.

Fig. 9 shows the emission and excitation spectra of the HDI-derivative. These spectra were taken under "stopped flow" conditions and the amount of HDI is 25 ng, corresponding to about 0.03 mg/m^3 for a 15 l air sample. The corresponding spectra for the TDI and MDI urea derivatives are, as expected, similar to those in Fig. 9. It is evident that by using fluorescence detection interference from UV-absorbing nonfluorescent compounds can be avoided. Because of the possibility to change excitation as well as emission wavelengths, certain fluorescent impurities can also be eliminated.

It is also possible to establish the identity of a peak in the fluorescence spectrum by running its emission and excitation spectra. However, decomposition products formed from the reagent cannot generally be distinguished by their spectra, which are similar to those of the ureas.

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