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CAPILLARY GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF COMPLEX MIXTURE OF ISOCYANATES AND AMINES

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SUMMARY

A capillary gas chromatographic method using nitrogen-selective detection was developed for the analysis of complex mixtures of isocyanates and amines in air. The isocyanate group was converted directly in the air sampling step into urethane by reaction with ethanol using potassium hydroxide as a catalyst. The amine group was converted into an amide using pentafluoropropionic anhydride in an extractive derivatization procedure. The complex pattern of air pollutants after thermal degradation of a polyurethane polymer, based on toluene diisocyanate (TDI) and 3,3′-dichloro-4,4′-diaminodiphenylmethane (MOCA), was investigated. Substantial amounts of amines, isocyanates and aminoisocyanates, molecules containing both an amine and an isocyanate group, were found. Consideration must be given to these findings when using current methods for isocyanate and amine determination. The detection limits for isocyanates, amines and aminoisocyanates, essentially depending on the nitrogen content of the molecule, were about equal and in the order of 40–80 fmol.

INTRODUCTION

Isocyanates and amines are the predominant pollutants in many workplace atmospheres and various methods for their determination have been developed.

Isocyanates are most frequently determined, after derivatization to urea derivatives, by high-performance liquid chromatography (HPLC) with UV[1–4], fluorescence[2,5,6] or electrochemical detection[7,8]. The choice of a strongly UV-absorbing or fluorescing agent in the derivatization step has permitted the trace analysis of both aromatic and aliphatic isocyanates. Aromatic amines present in samples have sometimes been simultaneously determined[4]. Direct analysis of free isocyanates by gas chromatography (GC) on packed columns using electron-capture detectors has been

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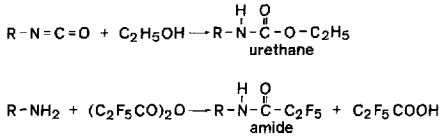
discussed[9,10]. A capillary GC method using electron-capture and nitrogen-selective detector has recently been reported[11].

GC has been the preferred method for the analysis of amines. Direct analyses of free amines[12–15] and also after a derivatization step have been described[16,17]. GC methods for total isocyanate monomer determination based on hydrolysis in acidic solutions have been presented[18–21]; they give the sum of the concentration of each isocyanate and its corresponding hydrolysed product.

Mixtures of isocyanates and amines in air may be very complex, especially following the thermal degradation of polyurethanes. The possible conversion of isocyanates to the corresponding primary amines by hydrolysis makes the sampling and analysis even more complicated. There is still a great need for methods that give high selectivity and low detection limits and where as many components as possible are determined simultaneously.

Here we describe a glass capillary GC method that permits the simultaneous determination of isocyanate monomers, primary and secondary amines and partially hydrolysed isocyanates. Air samples are collected in alkaline ethanol solutions and the sample work-up procedure includes two derivatization steps; in the first the isocyanate groups are derivatized with ethanol to form urethane groups and in the second the amine groups are derivatized with pentafluoropropionic acid anhydride to give the corresponding amide groups. The resulting toluene solution is finally analysed by capillary GC with nitrogen-selective detection.

The derivatization reactions are illustrated below.



R = alkyl or aryl

EXPERIMENTAL

Equipment

A Carlo Erba Fractovap Model 4160 gas chromatograph with on-column injection and a flame ionization detector and a Varian Model 3700 gas chromatograph, equipped with a Varian thermionic specific detector (TSD) and a Carlo Erba on-column injection system were used. Typical settings for the detector were as follows gas flow-rates, 4.0 ml/min of hydrogen and 180 ml/min of air; bead heating current, 5.3 scale divisions; bias voltage, −10 V; and detector temperature, 290°C. The carrier gas was helium at an inlet pressure of 1.0 kg/cm^2, dried over molecular sieve 5A and deoxygenated using an "Indicating Oxytrap" (Chrompack, Middelburg, The Netherlands). Chromatograms were recorded on Servogor Model 310 recorders, and a Hewlett-Packard Model 3390A integrator was used for peak evaluation. A Finnigan Model 4021 gas chromatograph–mass spectrometer was used in the electron impact (EI) and ammonia chemical ionzation (CI) modes with positive ion monitoring for structure confirmations. A Rotavapor-M (Büchi Laboratorium Technik, Plawil, Switzerland) connected to an aspiration pump was used for evaporation.

Column preparation

Duran 50 borosilicate glass capillary columns were drawn on a Carlo Erba GCDM Model 60 glass capillary-drawing machine and leached according to Grob and Grob[22]. The columns were dried by nitrogen purging for 2 h at 250°C. Deactivation was achieved by dynamic coating with a plug of 1,3-divinyltetramethyldisilazane followed by flame-sealing and thermal treatment at 350°C overnight. After rinsing with toluene, methanol and diethyl ether, PS-255 stationary phase (Fluka, Buchs, Switzerland) was applied by static coating from pentane solutions to produce a 0.75-μm stationary phase thickness. The stationary phase was then cross-linked with azo-*tert.*-butane according to Wright *et al.*[23].

Chemicals

The substances investigated were 2,4-toluene diisocyanate (2,4-TDI), 2,6-toluene diisocyanate (2,6-TDI), hexamethylene diisocyanate, isophorone diisocyanates, phenyl isocyanate, 1-naphthyl isocyanate, 2,4-toluenediamine (2,4-TDA), 2,6-toluenediamine (2,6-TDA), hexamethylenediamine, isophoronediamines, aniline, 1-naphthylamine, 3,3′-dichloro-4,4′-diaminodiphenylmethane and *o*-chloroaniline and the interfering substances considered were N-methylmorpholine, 1,4-diazabicyclo[2.2.2]octane (DABCO), dimethylethylamine, diethylamine, aniline and phenol. They were obtained from the following suppliers: E. Merck, Darmstadt, FRG (2,4- and 2,6-TDA hexamethylenediamine, 2,4-TDI, hexamethylene diisocyanate, isophorone diisocyanate, dimethylethylamine and 1-naphthyl isocyanate); Aldrich-Europe, Beerse Belgium (2,6-TDI) ICN Pharmaceuticals, Plainview, NJ, U.S.A. (isophoronediamine); Fluka, Buchs, Switzerland (N-methylmorpholine, DABCO and 1-naphthylamine); Mallinckrodt, St. Louis, MO, U.S.A. (aniline); and BDH, Poole, U.K. (diethylamine and phenol).

Isooctane and toluene were of glass-distilled grade from Rathburn Chemicals (Walkerburn, U.K.). Ethanol of spectroscopic grade was obtained from Kemetyl (Sweden). Pentafluoropropionic anhydride was obtained from Pierce (Rockford, IL, U.S.A.) and azo-*tert.*-butane from Alfa Products (Thiokol, Ventron Division, Danvers, MA, U.S.A.). The stationary phase PS-255 was obtained from Fluka and 1,3-divinyltetramethyldisilazane from Petrarch Systems (Bristol, PA, U.S.A.).

Procedure

Preparation of standards. Isocyanate standards (urethanes) were prepared by reaction of 30 mg of the isocyanates in 25 ml of ethanol at 60°C. For aromatic isocyanates a reaction time of 15 min was used and for aliphatic isocyanates 2 h. Standards were diluted with toluene prior to the GC analysis. The standards were stable for at least 3 weeks when stored in a refrigerator.

For amine standards (amides), 1 ml of toluene and 20 μl of pentafluoropropionic anhydride were placed in a test-tube containing 0.1 μmol of amine in 1 ml of 1 *M* phosphate buffer (pH 7) and the test-tube was immediately shaken vigorously for 1 min. The toluene layer containing the amide derivative was separated and stored in a refrigerator. The standards were stable for at least 3 weeks.

Sampling. An air sampling procedure was simulated as follows. A 10-ml volume of 0.2% (w/v) ethanolic potassium hydroxide solution was poured into a midget impinger flask. Isocyanates dissolved in isooctane (7 ng/μl) were injected into a glass

tube connected to the impinger inlet. The isooctane volume was varied between 20 and 100 μl. The tube was carefully heated, while air was drawn through it into the absorbing solution at a flow-rate of 1 l/min for 5 min. The concentration of isocyanates in the absorbing solution after sampling was in the range 14–70 ng/ml. The procedure was applied to 2,4- and 2,6-TDI and hexamethylene diisocyanate.

Work-up procedure before GC analysis. A 30-μl volume of phosphoric acid was added to 10 ml of absorption solution in an impinger flask. The solvent was slowly evaporated to dryness at 20°C during a period of *ca.* 15 min, then 1 ml of 1 *M* phosphate buffer (pH 7), 1 ml of toluene and 20 μl of pentafluoropropionic anhydride were added. The mixture was instantly shaken for 1 min, transferred into a small test-tube and the toluene layer analysed by GC.

RESULTS

Standards

Isocyanate derivatives (urethanes). Standards were prepared as described above and the conversion to urethanes was followed by GC. Aliquots of an ethanolic solution (0.5 μl) were removed and injected on-column on to a glass capillary column with chemically bonded PS-255 stationary phase and detected with a flame ionization detector.

The chromatograms in Fig. 1 illustrate the course of the uncatalysed reaction between hexamethylene diisocyanate and ethanol. At room temperature the reaction rate is slow (Fig. 1A). However, if the temperature is increased to 60°C the reaction is complete within 2 h (Fig. 1C). The reaction rates are, as expected, higher for aromatic than for aliphatic isocyanates. For 2,4- and 2,6-TDI less than 5 min are needed to complete the reaction. In all instances the reaction was complete within 2 h, hexamethylene diisocyanate having the lowest reaction rate.

Amine derivatives (amides). Extractive derivatization of amines with pentafluoropropionic anhydride is discussed elsewhere[24]. Complete reaction was achieved within 1 min. The amides formed were stable in toluene solution for at least 3 weeks at nmol/ml concentrations.

Sample preparation prior to GC analysis

Operations included are air sampling of isocyanates/amines, addition of phosphoric acid to the sampling solution (0.2% potassium hydroxide in ethanol), solvent evaporation, extraction with toluene and, for sample components containing primary amino groups, derivatization with pentafluoropropionic anhydride in connection with the extraction step.

Air sampling. The reaction between isocyanates and ethanol with ethanol as absorption medium on air sampling has been discussed by Nieminen *et al.*[4]. They showed that addition of 0.2% potassium hydroxide to the ethanol effectively catalysed the reaction with aromatic isocyanates and made side-reactions negligible. We found that the same applies to aliphatic isocyanates. To determine the influence of moisture and oxygen on the sampling of isocyanates/amines in alkaline ethanolic solution, the sampling period was varied between 5 and 20 min with an air flow-rate of 1 l/min, a relative humidity of about 50% and an absorption volume of 10 ml. No significant differences were found.

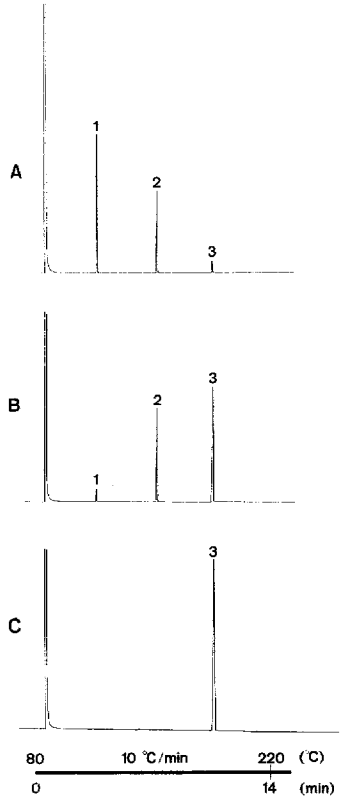


Fig. 1. Urethane formation from hexamethylene diisocyanate (1.2 mg/ml) in ethanolic solution. Chromatogram A was obtained after 40 min at 25°C, B after 30 min at 60°C and C after 120 min at 60°C. (1) Hexamethylene diisocyanate; (2) partially reacted hexamethylene diisocyanate; (3) totally reacted hexamethylene diisocyanate. On-column injection of 0.5 μl of ethanolic solution. Column: 10 m × 0.32 mm I.D. Duran 50 glass capillary, 1,3-divinyltetramethyldisilazane-deactivated, with PS-255 as the stationary phase; film thickness, 0.75 μm. Temperature programming as shown. Carrier gas: helium at 0.5 kg/cm^2. Flame ionization detection.

Addition of phosphoric acid. In order to neutralize the potassium hydroxide, about 15 μl of phosphoric acid are needed under the conditions described under Experimental. This gives satisfactory results for the analysis of the urethanes. If amines are to be analysed simultaneously, the amount of phosphoric acid is increased to 30 μl to prevent losses of amines during the evaporation step. A modification of the procedure with addition of phosphoric acid immediately after sampling for 5 min and after a delay period of 30 min before the work-up procedure did not give significant losses. This shows that the urethane formation reaction is complete within minutes in alkalinized ethanol.

Extraction. The extraction efficiency for the urethanes and amides was studied by shaking standards in toluene for 10 min with 1 *M* phosphate buffer (pH 7) and comparing the concentrations of the derivatives in the toluene layer before and after this operation. A 100% extraction efficiency was found for all isocyanate and amine derivatives.

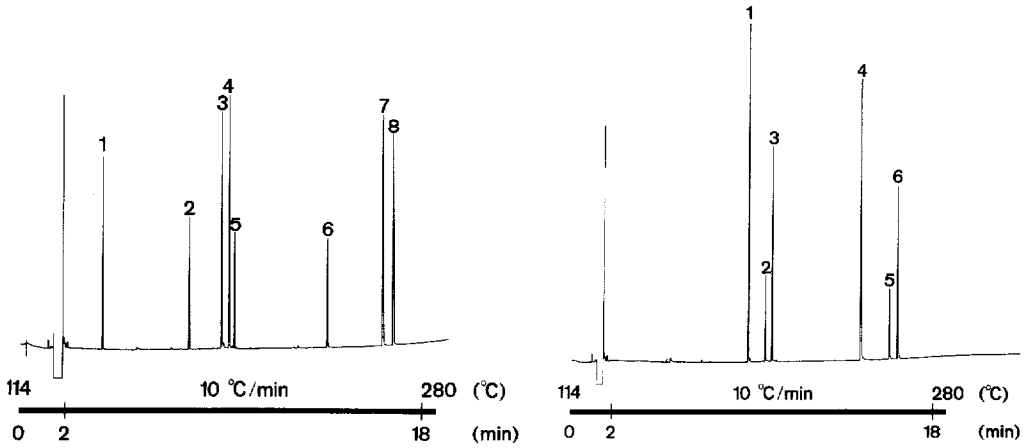


Fig. 2. Chromatogram of pentafluoropropionic derivatives of aromatic amines and ethanol derivatives of aromatic isocyanates (urethanes). On-column injection of 1 μl of a 4 pmol/μl toluene solution of derivatives of (1) aniline, (2) phenyl isocyanate, (3) 2,6-TDA, (4) 2,4-TDA, (5) 1-naphthylamine, (6) 1-naphthyl isocyanate, (7) 2,6-TDI and (8) 2,4-TDI. Column: 15 m × 0.32 mm I.D. Duran 50 glass capillary, 1,3-divinyltetramethyldisilazane-deactivated, with PS-255 as the stationary phase; film thickness, 0.75 μm. Temperature programming as shown. Carrier gas: helium at 1.0 kg/cm^2. Nitrogen-sensitive detector (Varian TSD) with bead heating current 5.3 scale divisions, bias voltage −10 V, detector temperature 290°C, hydrogen at 4.0 ml/min, air at 400 ml/min and nitrogen make-up gas at 5 ml/min. Attenuation: $4 \cdot 10^{-12}$ A f.s.

Fig. 3. Chromatogram of pentafluoropropionic derivatives of aliphatic amines and ethanol derivatives of aliphatic isocyanates (urethanes). On-column injection of 1 μl of a 4 pmol/μl toluene solution of derivatives of (1) hexamethylenediamine, (2 and 3) isomers of isophoronediamine, (4) hexamethylene diisocyanate, and (5 and 6) isomers of isophorone diisocyanates. Chromatographic conditions as in Fig. 2.

Chromatography

The chromatographic behaviour of the urethanes and amides is shown in Figs. 2 and 3. The good resolution obtained between urethanes and amides is important when both types of compounds occur simultaneously. The use of an apolar stationary phase with a relatively high film thickness offers the best resolution.

Quantification

Quantification was based on peak-height measurement and comparison with external standards. The overall yield did not significantly differ from 100% in any case when the work-up procedure was executed within 1 h after the sampling. The precision at a concentration of 0.7 ng/μl was *ca.* 5% for five samples. The contribution to the precision from the chromatographic run alone was typically less than 2% for both urethanes and amides with triple injections at a concentration of 400 pg/μl.

Air sampling of toluene diisocyanates, some of the most important isocyanates with respect to occupational health, was further studied according to the procedure described under Experimental. The variation of the peak height with concentration of 2,4-TDA and 2,4-TDI is shown in Fig. 4. The concentration range investigated, 140–700 pg/μl, corresponds to isocyanate concentrations in air of 0.4–2 times the

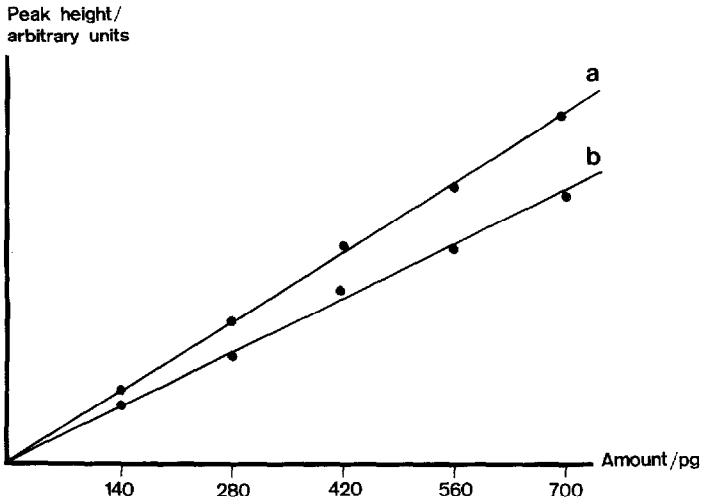


Fig. 4. Calibration plot for (a) 2,6-TDA and (b) 2,6-TDI as amide and urethane derivatives. Volume injected, 1 μl. Chromatographic conditions as in Fig. 2.

Swedish Threshold Limit Value (0.01 ppm, 5-min sampling period). A corresponding plot for 2,6-TDA and 2,6-TDI shows identical slopes and zero intercepts.

Detection limits

As the chromatographic behaviour of both urethanes and amides is good, the detection limits for the derivatives are similar, depending essentially on the nitrogen content of the derivatives when using a nitrogen-selective detector. It is about 80 fmol for substances with one nitrogen atom and about 40 fmol for those with two nitrogen atoms (1-μl injection, on-column), and decreases slightly with increasing retention times for the molecules eluted. For toluene diurethanes these figures correspond to 4 fmol.

Interferences

2,4- and 2,6-TDI and 2,4- and 2,6-TDA were chosen as model substances. The interfering substances investigated (see *Chemicals*) are expected to occur as pollutants in work atmospheres.

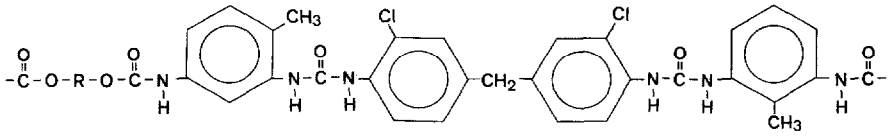
Air sampling of isocyanates was performed as described under Experimental. The amount of isocyanates corresponds to an air concentration of 0.01 ppm, which with an air volume of 5 l gives a concentration of 35 ng/ml in the 10-ml sampling solution (0.2% potassium hydroxide in ethanol). Toluenediamines were added to the sampling solution to give the same concentrations together with a 1000-fold relative molar amount of interfering substances. Air sampling, the work-up procedure and analysis as described under Experimental were performed within 4 h.

The yield of urethanes did not differ significantly from 100% in any instance, when compared with standards. Only with diethylamine as an interfering substance did we find a slight decrease (*ca.* 10%) in the yield of the amides. An increase in the amount of the reagent (anhydride) did not improve the yield. When the diethylamine

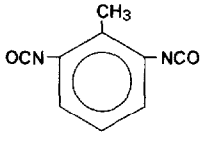
TABLE I

SCHEMATIC REPRESENTATION OF AN ADIPRENE POLYMER AND EXPECTED DEGRADATION PRODUCTS

The numbers of the compounds refer to the chromatogram in Fig. 5.

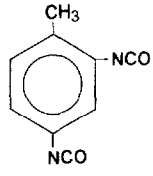


R = alkyl



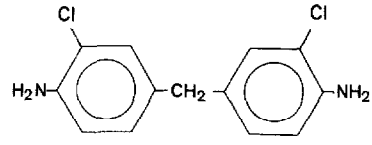
7

2,6-Toluene diisocyanate



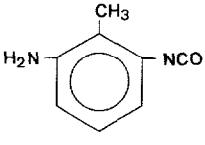
8

2,4-Toluene diisocyanate

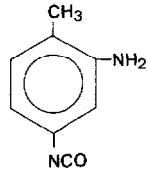


9

3,3'-Dichloro-4,4'-diaminodiphenylmethane

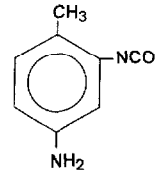


3-Amino-2-methylphenyl isocyanate

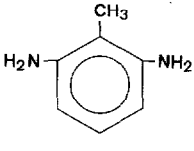


4 - 6

3-Amino-4-methylphenyl isocyanate

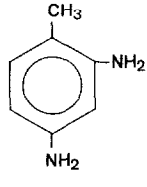


5-Amino-2-methylphenyl isocyanate



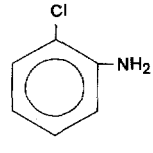
2

2,6-Toluenediamine



3

2,4-Toluenediamine



1

o-Chloroaniline

to isocyanate ratio was decreased by a factor of 10, the amides also gave a yield of 100%.

Stability test

In order to test the stability of the urethanes and amines present in the sampling

solution, the same procedure for analysis was used as in the interference test above. Model substances, sample concentrations and interfering substance concentrations were as above, except the diethylamine concentration, which according to the results above was decreased 10-fold. Solutions were allowed to stand for 3 weeks in daylight or darkness at room temperature (about 22°C).

We found the urethanes to be stable in all instances. However, the investigated toluenediamines were found to be stable for such a long period only in the absence of interfering substances. With interfering substances present, only small fractions (less than 10%) of the amines could be detected after derivatization to the corresponding amides.

Another problem with alkaline solutions containing interfering substances in large amounts is that these substances may decompose on standing, resulting in the occurrence of substances that interfere with the chromatographic separation. However, the urethanes appear late in the chromatograms, in contrast to most of the decomposition products emanating from interfering substances. Only in one instance, aniline, did an overlapping peak appear for 2,4-toluenediurethane. In this instance the peak height for the 2,6-isomer was unaffected. The 2,4-isomer is therefore probably also stable.

Application

Thermal degradation of polymeric material may occur in many situations, and the knowledge of the type and concentrations of the degradation products in air and hence the risks of exposure is very limited. The reason for this is mainly the complex pollutant pattern and the accompanying need for powerful analytical separation methods.

In this application we studied the thermal degradation of a polyurethane, Adiprene, formed by the reaction of a prepolymer of 2,4- and 2,6-TDI with 3,3′-dichloro-4,4′-diaminodiphenylmethane (MOCA) as curing agent. Possible degradation patterns have been discussed elsewhere[25,26]. The most important fragmentation products of occupational health interest to be expected are isocyanates, amines and degradation compounds containing both isocyanate and amine functional groups (see Table I).

Two polymers based on Adiprene L-42 and Adiprene L-325 (DuPont, Wilmington, DE, U.S.A.) were investigated. The thermal degradation experiment was performed as follows: 5 mg of the polymer were placed in a glass tube and air at a flow-rate of 1 l/min was led through the tube into a midget impinger containing 10 ml of alkaline ethanol absorption solution. The glass tube was heated from 20 to 350°C during a period of 10 min, which also was the total sampling time. The resulting samples were pre-treated and analysed by GC as described above.

Fig. 5 shows a typical chromatogram obtained using a nitrogen-selective detector. Thermal degradation of the polymers may result in three isomeric aminoisocyanates (see Table I). The amount of aminoisocyanates compared with the total amount of nitrogen-containing degradation products in the chromatogram was calculated to be in the order of 35%, assuming the same detector response per mole of substance. The corresponding fractional amounts were *ca.* 5% for TDA, 23% for TDI, 30% for MOCA and 7% for *o*-chloroaniline. The two Adiprene polymers gave the same patterns but with different relative amounts.

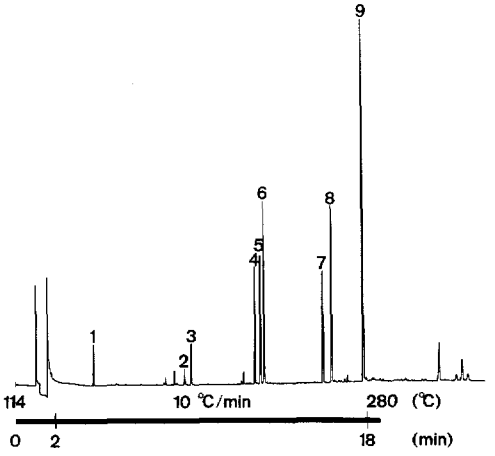


Fig. 5. Chromatogram of derivatized thermal degradation products from a polyurethane polymer (Adiprene). Amine groups derivatized with pentafluoropropionic anhydride and isocyanate groups with ethanol. On-column injection of 1 μl toluene solution of derivatives of (1) *o*-chloroaniline, (2) 2,6-TDA, (3) 2,4-TDA, (4–6) aminoisocyanates, (7) 2,6-TDI, (8) 2,4-TDI and (9) 3,3'-dichloro-4,4'-diaminodiphenylmethane. Compounds are illustrated in Table I. Attenuation: $32 \cdot 10^{-12}$ A f.s. Chromatographic conditions as in Fig. 2.

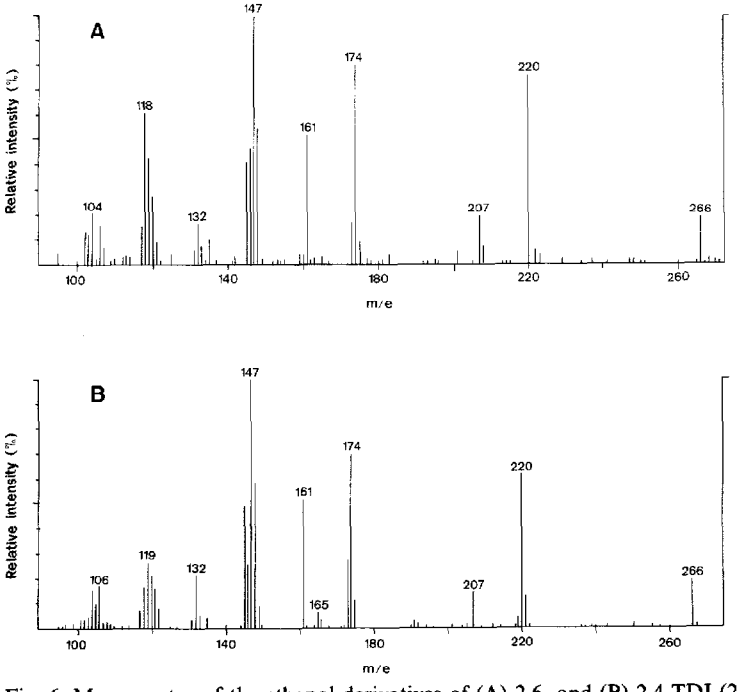


Fig. 6. Mass spectra of the ethanol derivatives of (A) 2,6- and (B) 2,4-TDI (2,6- and 2,4-toluene diurethanes) obtained by electron-impact ionization and positive ion monitoring.

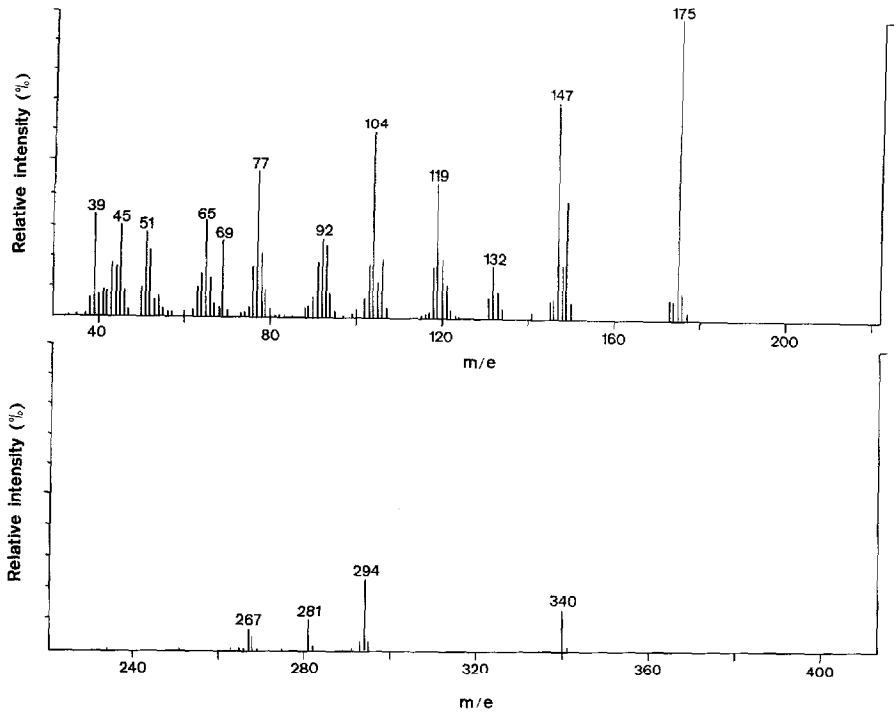


Fig. 7. Mass spectrum of ethanol and pentafluoropropionic derivatives of a monoaminotoluene monoisocyanate obtained by electron-impact ionization and positive ion monitoring (peak 4 in Fig. 5).

The peaks in Fig. 5 were identified by comparison with standards and further confirmed by mass spectrometry. A complementary approach is to use a dual detection system with nitrogen-selective and electron-capture detector[16].

Mass spectrometry

The mass spectra of amides formed by the reaction between pentafluoropropionic anhydride and the amines in Fig. 5 have been discussed elsewhere[27]. Mass spectra of the present diurethanes and of mixed compounds containing both urethane and amide groups are briefly discussed below.

Electron-impact (EI) mass spectra of the two 2,4- and 2,6-toluene diurethanes are shown in Fig. 6. The fragmentation patterns for the two isomers are very similar with the molecular ion M with *m/e* 266. Mass spectra for the monoaminotoluene monoisocyanate derivatives were obtained utilizing both electron impact as well as chemical ionization (CI) with ammonia. Figs. 7 and 8 show mass spectra for one of the derivatives (peak 4 in Fig. 5) in the EI and CI modes. The mass spectra for all these derivatives are similar, with abundant ions for EI with *m/e* 340, 294, 175 and 147 and for CI with *m/e* 358, 341 and 279. The peak with *m/e* 340 in EI corresponds to the expected molecular weight. According to ref. 28, characteristic peaks in the ammonia CI spectrum are (M + H) and (M + NH_4), which with a molecular weight of 340 will give the peaks obtained with *m/e* 341 and 358, respectively.

Typical fragmentation peaks of urethanes when using the EI mode are an

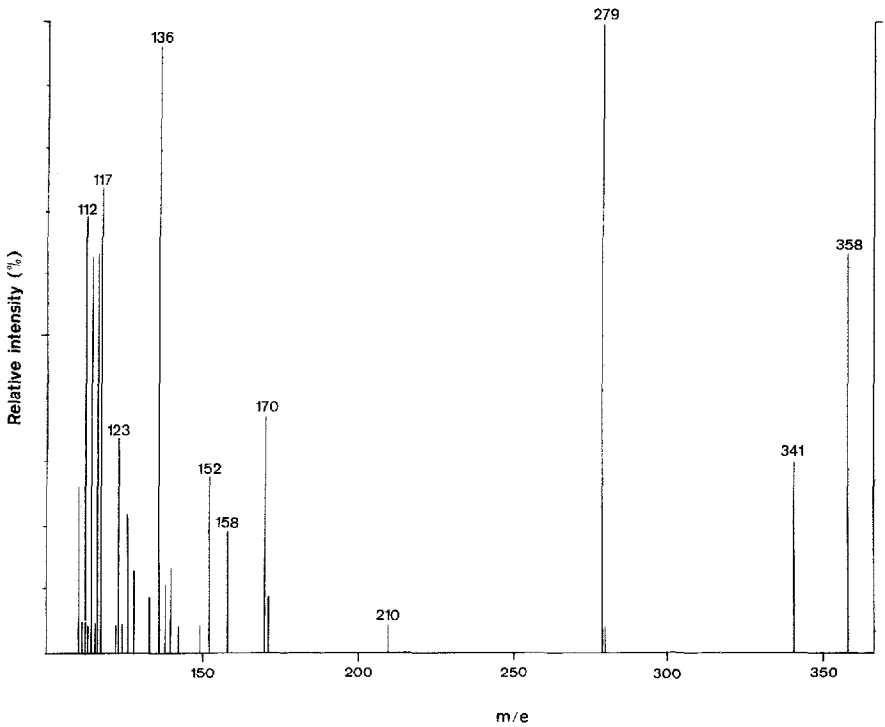


Fig. 8. Mass spectrum of ethanol and pentafluoropropionic derivatives of an aminoisocyanate obtained by chemical ionization with ammonia and positive ion monitoring (peak 4 in Fig. 5).

(M − 46) peak with the loss of C_2H_5OH and an (M − 59) peak with the loss of CO_2 and CH_3· (ref. 29). These fragments are found in the EI spectra of 2,4- and 2,6-toluene diurethanes in Fig. 6 at *m/e* 220 and 207, respectively, and also in the spectra of the aminoisocyanates (see Fig. 7) at *m/e* 294 and 281, respectively. The loss of C_2H_5OH in phenylurethane results in phenyl isocyanate[29]. The loss of two C_2H_5OH groups from toluene diurethanes should give toluene diisocyanates at *m/e* 174 (M − 92). This fragment is also found and gives one of the most abundant peaks. The occurrence of this fragment is probably due to both thermal- and EI-induced fragmentation[29]. In a similar way a simultaneous fragmentation of amide and methane groups in the aminoisocyanate derivatives with a loss of C_2F_5 from the amide group and a loss of C_2H_2OH from the urethane group will give the peak with *m/e* 175 in Fig. 7.

C_2F_5 fragments with *m/e* 119 and CF_3 fragments with *m/e* 69 have been observed previously in the EI mass spectra of pentafluoropropionic diamides of 2,4- and 2,6-TDI[27]. These fragments also appear in the spectrum of the aminoisocyanates. However, it should be noted that a peak with *m/e* 119 is also present in the spectra of the diurethanes in Fig. 6A and B.

DISCUSSION

The hydrolysis of isocyanates and thermal degradation of polyurethanes has

been studied in some detail over several years in our laboratories[26,30,31] and the work reported here is a continuation of these investigations.

The method described allows the simultaneous determination of aliphatic and aromatic isocyanates and amines and of aminoisocyanates (see Fig. 5). In the HPLC method using UV detection described by Nieminen *et al.*[4], where isocyanates are determined as urethanes and amines as free amines, only UV-absorbing compounds can be simultaneously determined. In other HPLC methods based on derivatization of the isocyanate group with strongly UV-absorbing or fluorescing agents, aliphatic isocyanates can also be determined, whereas aliphatic amines still remain undetected and aromatic amines often co-elute with the reagent.

A distinct advantage of the present method is the high resolution and the possibility of mass spectrometric detection, which greatly facilitates the identification of eluted compounds.

The simultaneous occurrence of isocyanates and corresponding fully hydrolysed amines in air has been investigated previously[32]. Discrimination between the two types of substances was indirectly accomplished by a combination of two analytical methods. The isocyanates were determined by HPLC after derivatization and UV detection and the sum of the isocyanates and corresponding amines by GC as perfluoro fatty acid amides after sampling in acidic solutions. This approach may cause errors, however, if aminoisocyanates are present as these are hydrolysed to diamines. On thermal degradation of polyurethanes, the amounts of aminoisocyanates may widely over-range those of diamines. When such samples are collected in acidic solutions, the concentrations of diamines will obviously be markedly overestimated.

The roughly equal sensitivity for all derivatives with the GC method using nitrogen-selective detection described here compares favourably with that obtained by HPLC, where the sensitivity varies with the type of substance. The detection limits are comparable to those obtained by HPLC. Further, the selectivity with the nitrogen-selective detector is superior to that with HPLC detectors.

The results obtained in the interference and stability tests show that the method presented here can be used as a routine method for isocyanate determination. Nieminen *et al.*[4] also found that the isocyanate derivatives showed excellent stability in the sampling solution. The matrix in their samples, however, was not described. For amine determinations the sample storage is critical. We have shown that if the sample work-up procedure starts shortly after the completed sampling period, as much as a 1000-fold molar amount of tertiary amines may be present without disturbing the determination of the primary amines as amide derivatives. However, after storing such solutions in darkness at room temperature for 3 weeks only about 10% of the initial amine concentrations could be found. Further improvements directed towards better stability of the amines in the sampling solution are necessary if this method is to be used as a routine method for the determination of primary and secondary amines, as the period between sampling and analysis may often be several weeks. To avoid side-reactions, the reaction rate between isocyanates and ethanol was increased by using potassium hydroxide. Nieminen *et al.*[4] have discussed the merits of this catalyst, and other catalysts have been discussed by Farkas and Mills[33]. The choice of another catalyst such as an organotin compound may enhance the stability of amines in the absorbing solution.

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