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ANALYSIS OF ORGANIC ISOCYANATES USING CAPILLARY SUPERCRITICAL-FLUID CHROMATOGRAPHY

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SUMMARY

Capillary supercritical-fluid chromatography (CSFC) is shown to provide high-resolution separations of a wide variety of di-, tri- and polyisocyanates, including derived products such as dimer, trimer, urea, biuret, carbodiimide, phenol-blocked, thiophosphoric, carbamate and thiocarbamate isocyanates. CSFC is superior to any other available separation technique for many isocyanates. Derivatization is not necessary with a carbon dioxide mobile phase. Significant changes in selectivity of diisocyanate separations were effected by variations in temperature and use of methyl, biphenyl and octyl methylpolysiloxane stationary phases. Operating temperatures of up to 100°C could be used. With neat carbon dioxide as the mobile phase, the applicable mass range had an upper limit of 500–2000 g mol^{-1}, depending on sample structure and composition.

INTRODUCTION

Polyurethane manufacturing is centred around the reactions of isocyanates with various alcohols. The reactivity of isocyanates and the thermal lability of many of the derived products makes their analysis difficult. The types of isocyanates in use range from the low-molecular-weight to very high-molecular-weight polymers, and also monomeric and polymerized derivatives such as ureas, dimers and trimers, blocked isocyanates and prepolymers of an isocyanate and polyol.

Exposure to low levels of isocyanates can cause serious effects on respiratory and other physiological systems in humans[1]. Therefore, trace analytical techniques have been, and continue to be, extensively studied, with primary emphasis on chromatographic-based methods. Another level of analysis is the screening, or quality control, of bulk product material. Although the synthesis of many monomeric isocyanates can be well controlled, reactions leading to many derived products often yield

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complex mixtures that cannot be adequately characterized by present separation techniques.

The trace analysis of isocyanates in air was recently reviewed[1]. Analysis at trace levels is usually for the determination of the volatile, low-molecular-weight isocyanates that present the greatest exposure hazards. Higher molecular weight isocyanates can be adsorbed on to dust particles, or be present in aerosols, and thereby present health hazards. Allowable exposure limits have recently become based on total isocyanate group concentrations[1], thus including these higher molecular weight isocyanates. Trace chromatographic analysis of isocyanates requires high sensitivity, with sample solution concentrations of the order of 1–100 ppb[2] in high-performance liquid chromatography (HPLC). At these low levels the stability of the isocyanates is a primary concern. To prevent reaction between isocyanates and atmospheric moisture or other compounds that may be present, air samples are usually drawn through a derivatizing/absorbing solution. Derivatization is necessary for HPLC analyses owing to possible reaction with mobile phase components such as water and alcohols.

At the screening level, complications inherent in trace analysis are not present. Both HPLC and thin-layer chromatography are used to analyse derivatized samples, but only with a limited number of the higher molecular weight polymeric isocyanates[1]. Gel permeation chromatography (GPC) provides the only means for analysing many of the higher molecular weight isocyanates. However, moisture, impurities and stabilizers in the GPC mobile phase are potential problems. The low resolution of GPC does not provide much detail about polymeric distributions[3]. Isomeric separations are normally not possible.

The thermodynamic and transport properties of supercritical fluid mobile phases produce higher efficiency separations than are possible in HPLC, and also possess solvating properties not present in gas chromatography (GC). When a low-critical-temperature fluid is used as the mobile phase, such as carbon dioxide (T_c = 31°C), thermally labile compounds may be chromatographed in addition to high-molecular-weight samples. Use of carbon dioxide as the mobile phase should eliminate the need for derivatization of reactive samples such as isocyanates, which is a significant advantage over HPLC. The inherently high resolution of capillary columns when used in supercritical-fluid chromatography (SFC) results in a system that can separate a wide variety of complex mixtures. Most detection systems used in HPLC or GC have been interfaced with SFC. A carbon dioxide mobile phase can be used with a standard GC flame ionization detector, thus allowing the analysis of non-chromophoric samples, a significant advantage over HPLC.

The analysis of toluene diisocyanate (TDI) by capillary column SFC (CSFC) has been reported[4]. The same chromatogram was subsequently published[5] with three peaks indicated to be the dimer, trimer and tetramer of TDI. The monomer and dimer were analysed in this study. No trimer was available for inclusion in this study and, whereas polymerized forms of isocyanates exist, no tetramer structure of TDI has been defined in the literature.

Packed-column SFC (PSFC) is also an extremely powerful separation technique and can solve many analysis problems faster and with higher resolution than is possible with HPLC. However, with isocyanate samples, PSFC may not be a viable alternative, for two reasons. First, the packed columns have a high concentration of surface silanol groups which could react with the isocyanates. Second, an organic

solvent, usually an alcohol, is typically added to the mobile phase to cover these active sites in the column. Such a modifier could also react with the isocyanate samples. However, use of a non-reacting solvent such as a chlorinated hydrocarbon or acetonitrile may be feasible.

The advantageous properties of supercritical fluids were exploited in this study to develop an improved, screening-level separation technique. The effects of temperature and impurities, in both the sample and the mobile phase, were studied with regard to both trace- and screening-level analyses. A wide variety of isocyanate and isocyanate-derived samples were chromatographed. Comparisons with results from GPC were made to estimate the extent of sample elution in CSFC. Samples were tested for thermal stability in GC analysis.

EXPERIMENTAL

Two CSFC instruments were used, one constructed in our laboratories and the other a commercially available instrument. All analyses, except of the IPDI–urea (Fig. 9A), the IPDI–trimer (Fig. 11A) and Desmodur HL (Fig. 11B) were performed with the former instrument.

The former instrument consisted of a high-pressure syringe pump (Model 8500, Varian Instruments, Walnut Creek, CA, U.S.A.) modified for pressure control[6] and a chromatograph oven (Model 4100, Carlo Erba, Milan, Italy) equipped with a flame ionization detector. The injection system consisted of an electrically actuated HPLC sampling valve (Model C14W, Valco, Houston, TX, U.S.A.), with an internal sample loop of 0.2 μl and 1-s injection time, coupled to a CSFC splitter (Scientific Glass Engineering, Ringwood, Australia). The carbon dioxide splitting ratio was approximately 20:1. The valve was fitted with a cooling device to maintain the valve temperature at about 15–20°C. A 2-μm pore screen filter was installed in the sample loading port of the injection valve to prevent contamination or plugging of the chromatographic system by particles from the sample or syringe. The carbon dioxide mobile phase used was 52-grade (99.9992%, Carba Gas, Basle, Switzerland), without dip tube. A neutral alumina trap was installed between the tank and the pump. It consisted of 1.5 m of 1/4 in. I.D. stainless-steel tubing fitted with frits on each end. Valves placed on each end allowed the isolation of the trap from atmospheric moisture following activation at 200°C with a nitrogen purge overnight. The trap was flushed several times with carbon dioxide before filling the pump.

The commercially available CSFC system was a Model 601B from Lee Scientific (Salt Lake City, UT, U.S.A.). It consisted of a syringe pump, oven and flame ionization detector. SFC-grade carbon dioxide (Scott Gases, Plumsteadville, PA, U.S.A.) was used: the cylinder did not have a dip tube.

Columns were 100-μm I.D. deactivated fused silica coated with different stationary phases (Lee Scientific). For all analyses, except the selectivity tests with low-molecular-weight diisocyanates (Figs. 4 and 5), the stationary phase was a 100% methylpolysiloxane (SB-Methyl-100, Lee Scientific) of 0.5-μm film thickness. The stationary phases in Figs. 4 and 5 were biphenyl–methylpolysiloxane (30:70) (SB-Biphenyl-30, Lee Scientific) of 0.25-μm film thickness, and *n*-octyl–methylpolysiloxane (50:50) (SB-Octyl-50, Lee Scientific) of 0.5-μm film thickness, respectively. Short lengths (*ca.* 5 m) were used to decrease the analysis time.

Pressure restriction and column flow in both instruments were regulated with a ceramic frit restrictor (Lee Scientific) (20 cm × 50 μm I.D.) with an original frit length of 2 cm. The frit length was reduced to about 1 cm to provide a linear velocity of about 1 cm s^{-1} with the usual initial programming conditions. Experiments with a 7 μm I.D. capillary restrictor showed no differences in chromatographic profiles. Although the frit restrictor had nearly 10 cm of non-deactivated surface inside the oven, and another 8–10 cm in the detector heated zone, no adsorption was observed.

Data were acquired and processed with Nelson Analytical (Cupertino, CA, U.S.A.) software. The sampling rate for all analyses was 1 or 2 points per second.

Injection solution concentrations were typically 0.02–1.0% in dichloromethane (HPLC grade). A few percent of tetrahydrofuran in dichloromethane was required for complete dissolution of 1,4-phenylene diisocyanate.

The low-molecular-weight diisocyanates were obtained in high purity from various local distributors: isophorone diisocyanate, 2,4-toluene diisocyanate, 1,6-hexane diisocyanate and 1,3-xylylene diisocyanate from Fluka (Buchs, Switzerland), trimethylhexane diisocyanate from Merck (Zurich, Switzerland) and 2,6-toluene diisocyanate and 1,4-phenylene diisocyanate from Aldrich (Steinheim, F.R.G.). Technical grade liquid 4,4′-diphenylmethane diisocyanate was obtained from Merck. All samples of the Desmodur series were obtained from Bayer (Leverkusen, F.R.G.). The Isonate 143L sample was obtained from Upjohn (Kalamazoo, MI, U.S.A.). H2921 (IPDI–urea), T1890/100 (IPDI-trimer) and BF1540 (IPDI–dimer) samples were obtained from Hüls (Marl, F.R.G.). The thiocarbamate adducts are produced by Ciba-Geigy. The idealized or proposed structures are shown in the figures.

Linear density programming was used in all analyses. The programming parameters for analysis of low-molecular-weight diisocyanates (Figs. 2–4) were 5-min initial-density hold time, initial densities (g ml^{-1}) of 0.25 (50°C), 0.18 (75°C) and 0.15 (100°C), 0.01 g ml^{-1} min^{-1} programming rate and a final density of 0.5 g ml^{-1}. All other analyses were made with a density programming rate of 0.03 g ml^{-1} min^{-1} from 0.2 to 0.7 g ml^{-1} after a 5-min initial time (100°C in all instances), except for the Desmodur HL sample (Fig. 11B), which had a final density of 0.75 g ml^{-1}. Final-density hold times were 5–15 min.

GPC analyses were performed with a tetrahydrofuran mobile phase and a polystyrene column. Most of the samples were analysed, except for the low-molecular-weight diisocyanates. Representative gel permeation chromatograms of four complex mixtures are discussed below.

RESULTS AND DISCUSSION

Mobile phase impurity concentrations

Moisture in the chromatographic system, especially in the mobile phase, could lead to reaction with an isocyanate sample. This is clearly detrimental to trace analysis but, depending on the conditions and relative concentrations, may not be significant for screening-level analyses. A comparison was made between impurity levels in a carbon dioxide mobile phase and expected peak concentrations for the two analysis levels, trace and screening (Table I). The peak concentrations can vary by an order of magnitude or more depending on the column dimensions, analysis conditions and retention characteristics.

TABLE I

COMPARISON OF IMPURITY LEVELS IN CARBON DIOXIDE MOBILE PHASE WITH SOLUTE CONCENTRATION

Analysis level	*Solute concentration*[a]		*Carbon dioxide impurities (ppm)*[b]		
	Injection solution	*Peak*[c] *(ppm)*	H_2O	O_2	CO
Screening	1%	100	3	2	5
Trace	10^{-2} ppm	10^{-4}	3	2	5

[a] Assuming a phase ratio of 50 (*e.g.*, 0.5 μm d_f × 100 μm I.D.), capacity factor (k) of 2, injection volume 0.2 μl.

[b] SFC-Grade, Scott Specialty Gases.

[c] Values are not adjusted to account for split injection.

At the screening level the peak concentration is about 100 times that of water and other impurities and would seem to pose few problems. The trace level represents the detection limits of one of the most sensitive HPLC methods for the determination of TDI in air. The method[2] involves both a pre-concentration column and a large injection volume. In this instance the mobile phase impurity concentrations are 1000 times higher than the solute.

Operating temperature

Generally in CSFC it is desirable to operate at as high a temperature as possible in order to decrease the mobile phase viscosity and reduce the elution density, thereby increasing diffusion and obtaining less peak broadening. As many reactions of isocyanates can be driven by heat[7–9], an assessment of the effect of temperature on chromatographic integrity was made. The operating temperature may be a factor in various reactions of isocyanates such as polymerization, dimerization, trimerization, degradation and dissociation. Also, reactions with impurities may be favoured at certain temperatures.

A high-purity sample of 2,4-TDI was chromatographed at 50–100°C with *n*-alkane internal standards. The internal standards were C_{12} and C_{15}, which eluted before and after the TDI, respectively, with baseline resolution at all temperatures. The injection solution concentration was approximately 0.2% in dichloromethane, the concentration of internal standards being slightly higher. Table II lists the ratios of peak areas of the internal standards to 2,4′-TDI in 10°C increments. Clearly, no significant changes occurred in this range. These results contradict a report of dimer and trimer formation above 60–70°C in CSFC[10]. Dimer and trimer formation are reported to be catalysed by heat[7,8,11]; however no details or specific temperatures were reported. The preparation of dimers and trimers is usually performed with the aid of a catalyst[9,12–14]. Underivatized 2,4-TDI elutes at about 132°C in capillary GC with no detrimental effects on quantitation at trace levels[15].

Consideration must be given to two factors in the interpretation of such temperature-dependent results. First, the impurities remaining in isocyanate samples from the manufacturing processes are many and varied. With TDI, they include cyclic and linear ureas, biurets and some higher polyurets and chlorine-containing by-prod-

TABLE II

STABILITY OF 2,4-TDI IN CSFC AT VARIOUS OPERATING TEMPERATURES

Temperature (°C)	*Peak-area ratio*[a]	
	C_{12}/TDI	C_{15}/TDI
50	1.22	1.44
60	1.20	1.43
70	1.21	1.43
80	1.20	1.42
90	1.23	1.42
100	1.23	1.42

[a] *n*-Alkane internal standards.

ucts of the phosgenation steps[16]. If a sample has higher levels of these impurities, then the possibilities for reactions are also greater. Second, the presence of impurities in the mobile phase could also lead to reactions. As described above, the solute concentration relative to mobile phase impurities is important and may pose problems in trace analysis. A different TDI sample, Desmodur T100, apparently contained a few percent of the dimer and a few other impurities, whereas the high-purity TDI sample contained only a nearly undetectable amount of dimer (signal-to-noise ratio 2:1).

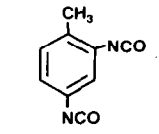
The technical-grade MDI was analysed over a wider temperature range (up to 140°C), although without a detailed internal standard quantification study. No noticeable changes occurred in the profile up to 100°C, except for the expected better peak shape. The temperatures above 100°C may have resulted in decomposition or polymerization.

Selectivity of diisocyanate separations with stationary phase and temperature

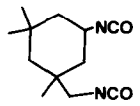
Several common diisocyanates were chromatographed with three stationary phases and at three temperatures. The changes in both peak width and selectivity were significant. The structures are shown in Fig. 1; however TDI, IPDI, and THDI are usually isomeric mixtures. Pure 2,4-TDI was obtained, but formulations are usually 80:20 or 65:35 mixtures with 2,6-TDI, which was also chromatographed. The THDI sample was a mixture of 2,2,4- and 2,4,4-trimethyl isomers. Similarly, the IPDI sample was a mixture of *cis* and *trans* isomers. Nine distinct diisocyanates were present in the sample mixture. Although it is unlikely that all or even most of these diisocyanates would be present in the same sample, several polyisocyanates are based on the combination of two of these, for example TDI and HDI. It is nonetheless advantageous to achieve the separation of as many as possible. No separation of 2,4- and 2,6-TDI was achieved under any conditions. In the following discussion, TDI refers to the coeluting peaks of these two isomers.

Using the non-polar 100% methyl stationary phase, HDI coeluted with the TDI isomers at all temperatures (Fig. 2). These two diisocyanates are used to form a polyisocyanate, Desmodur HL, which was included in this study. The second isomer of THDI and the first isomer of IPDI were slightly separated at 50°C, were well separated at 75°C and had baseline resolution at 100°C.

The biphenyl–methyl (30:70) stationary phase is considered to be a polarizable



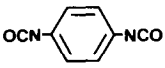
2,4–Toluene
Diisocyanate (TDI)



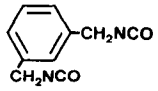
Isophorone
Diisocyanate (IPDI)

1,6–Hexane
Diisocyanate (HDI)

2,2,4–Trimethylhexane–
1,6–Diisocyanate (THDI)



p–Phenylene
Diisocyanate (PDI)



m–Xylylene
Diisocyanate (XDI)

Fig. 1. Structures of low-molecular-weight diisocyanates.

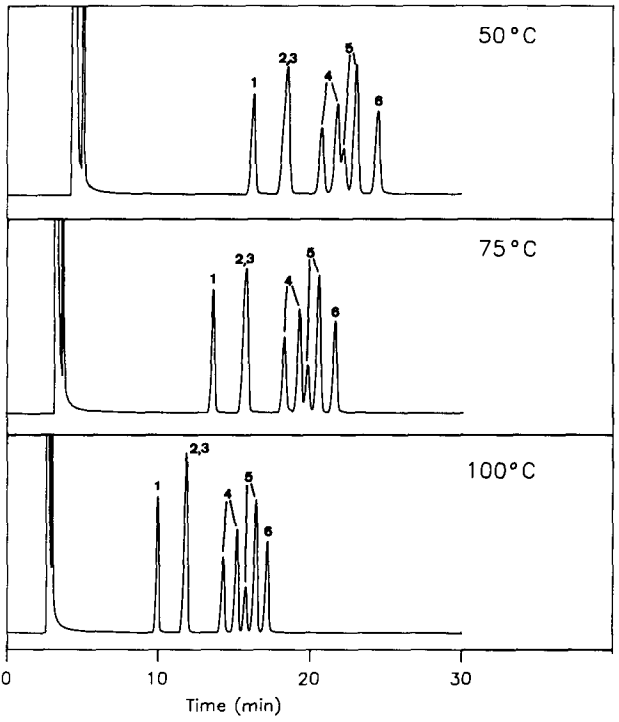


Fig. 2. CSFC traces of a mixture of low-molecular-weight diisocyanates at different temperatures using a 100% methyl stationary phase. Peaks: 1 = PDI; 2 = 2,4- and 2,6-TDI: 3 = HDI; 4 = THDI; 5 = IPDI; 6 = XDI.

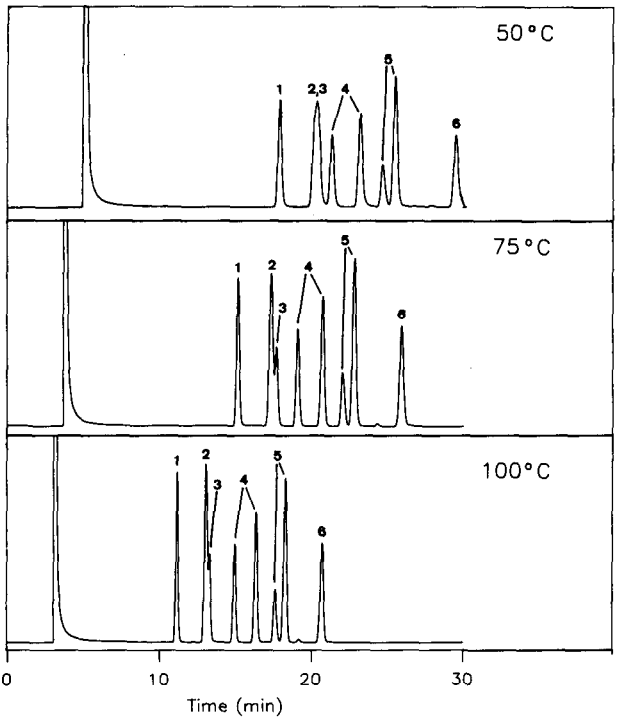


Fig. 3. CSFC traces of a mixture of low-molecular-weight diisocyanates at different temperatures using a biphenyl–methyl (30:70) stationary phase. Peaks as in Fig. 2.

phase [17]. In general, the retention was longest with this stationary phase relative to the other stationary phases (Fig. 3), even though the film thickness was half that of the other stationary phases under study. TDI and HDI again coeluted at 50°C. All other diisocyanates were well separated. At 75°C, HDI was slightly separated from TDI, possibly sufficient for quantitation. At 100°C the resolution of TDI and HDI was poorer than at 75°C.

At 50°C, with an *n*-octyl–methyl (50:50) stationary phase, PDI and HDI were slightly separated, but the resolution may be adequate for quantitation (Fig. 4). TDI and the first isomer of THDI almost coeluted and may yield poor quantitative data. The second isomer of IPDI overlapped slightly with XDI. At 75°C, there was baseline resolution of PDI and HDI, and also between the second THDI isomer and TDI. In contrast, the second IPDI isomer and XDI had poorer resolution, but possibly adequate for quantitation. At 100°C the resolution of all peaks improved, except for the second IPDI isomer and XDI, which coeluted.

The retention behaviour of HDI relative to the other diisocyanates, using the *n*-octyl stationary phase, was interesting and unexpected. As HDI is the most linear of these diisocyanates, it was expected that its retention would increase relative to the other branched alkyl or aromatic diisocyanates. Instead, its retention decreased relative to the other diisocyanates. A possible explanation is that HDI in supercritical

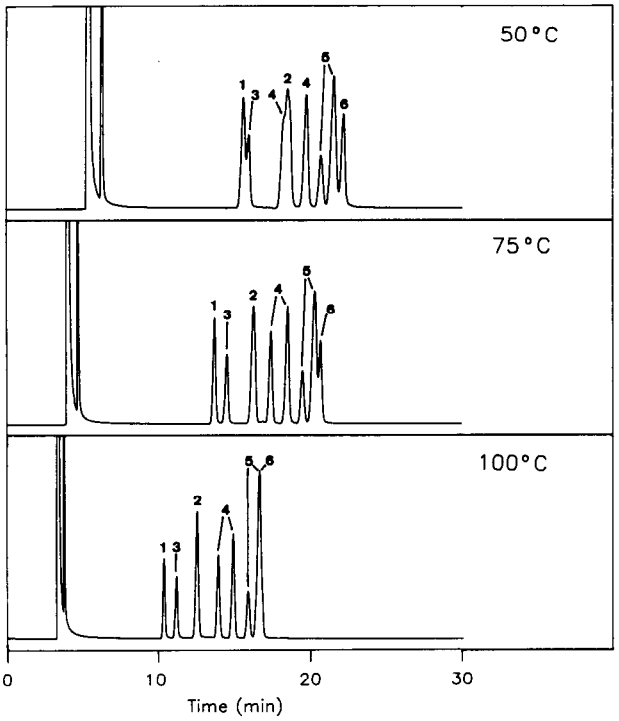


Fig. 4. CSFC traces of a mixture of low-molecular-weight diisocyanates at different temperatures using an *n*-octyl–methyl (50:50) stationary phase. Peaks as in Fig. 2.

solution is not a linear molecule but conforms to another structure which could have a lower relative affinity for the stationary phase.

In general, as the temperature increased the peak widths decreased, as expected. Resolution can also be affected by the mobile phase linear velocity, injection pressure and density, programming rate(s) and column inner diameter and length. Not only have pressure and density programming been demonstrated in CSFC with single-component mobile phases, but also simultaneous density–temperature[18,19] and constant density–temperature[19,20] programming. These features were not utilized in this study, but the former is available in most commercially available CSFC instruments.

MDI-based isocyanates

Recently, 4,4′-diphenylmethane diisocyanate (MDI) and other higher molecular weight isocyanates have been increasingly used as alternatives to the more volatile low-molecular-weight diisocyanates to reduce health hazards. Pure MDI is a solid at room temperature. This fact poses problems in polyurethane manufacture which can be overcome by using MDI modified to remain as a liquid at room temperature. Liquid MDI usually takes one of two forms. The unpurified product containing a series of higher oligomers, as shown in Fig. 5, can be used (polymeric MDI). Alternatively, MDI can be converted into a carbodiimide in the presence of special cata-

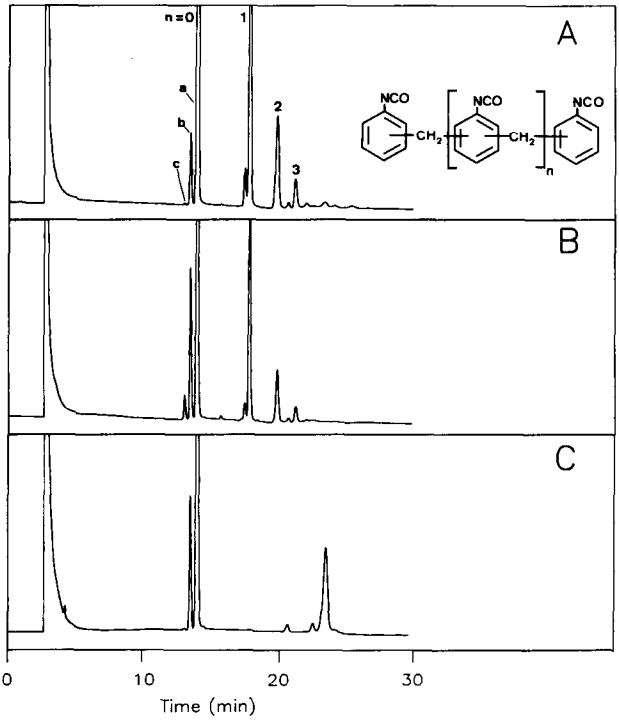


Fig. 5. CSFC traces of liquid MDI products. (A) Technical-grade MDI; (B) Desmodur VL; (C) Isonate 143L. Isomers: (a) 4,4′-MDI; (b) 2,4′-MDI; (c) 2,2′-MDI.

lysts[12,16,21] and added to pure MDI to produce a liquid. Both types of liquid MDI were analysed in this study.

Three samples of liquid MDI were included in this study. The technical-grade MDI and Desmodur VL samples were polymeric MDI, whereas Isonate 143L was a carbodiimide-modified MDI. These three samples were chromatographed at 100°C (Fig. 5). Differences in isomeric and oligomeric compositions were readily apparent. The first grouping of peaks corresponds to MDI, in the polymeric structure $n = 0$. It is known that the major product is 4,4′-MDI, and the 2,4′- and 2,2′-MDI isomers are present in smaller amounts[7,16]. The chromatogram of Desmodur VL (Fig. 5B) provides the best example of the presence of these isomers. Assuming an elution order of 2,2′-, 2,4′-, 4,4′-MDI, then the peak areas correspond to the approximate relative concentrations of the isomers. Oligomers of the polymeric MDI series could be detected up to $n = 4$ or 5, corresponding to molecular weights of 774 and 905 g mol^{-1}. Other peaks were also present and may be alkylated derivatives of the oligomers. Also, one of the peaks may be the dimer of 4,4′-MDI, which can form on standing at room temperature[7,9,16]. Separate homologous series apparently begin with the 2,4′- and 4,4′-MDI oligomers. However, the retention times of the two series converge at $n = 2$, although at 50°C the $n = 2$ peaks could be slightly separated. Such detailed analysis of isomeric distributions is not possible using GPC (Fig. 6).

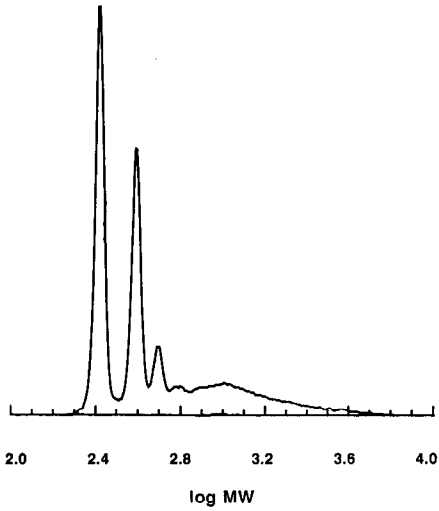
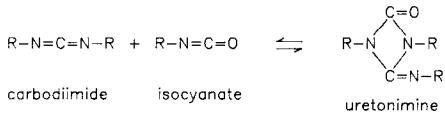


Fig. 6. GPC trace of a liquid MDI product.

As described above, MDI can be converted into a liquid by the addition of the corresponding carbodiimide. At room temperature the carbodiimide is in equilibrium with the corresponding uretonimine formed with free MDI:



No specific information was found in the literature regarding the temperature dependence of the carbodiimide–uretonimine equilibrium, other than the general statement that at higher temperatures the uretonimine dissociates into isocyanate and carbodiimide[16,22,23]. The Isonate 143L sample was initially chromatographed at 100°C (Fig. 5C), but the question remained of whether the peak eluting at higher density (23 min) was the carbodiimide or the uretonimine. The first two peaks corresponded to those of the other MDI samples and are therefore the 2,4′- and 4,4′-MDI isomers. The peak at 23 min was tentatively identified as the carbodiimide. The sample was chromatographed from 35 to 175°C to determine if the suspected carbodiimide peak was in fact a uretonimine. If the carbodiimide were in equilibrium with the uretonimine in the mobile phase, then an increase in temperature should shift the equilibrium towards the carbodiimide, thereby changing the peak-area ratios. The ratio of the area of the suspected carbodiimide peak to that of the 2,4′-MDI peak remained constant up to 100°C, indicating no changes in the suspected carbodiimide. Above 100°C the chromatographic profile changed and additional peaks appeared, and above 150°C the carbodiimide was no longer present. These results indicated that the uretonimine was not present in the Isonate 143L sample when eluted from the column. However, it is possible that the uretonimine was not soluble in carbon di-

oxide and therefore did not elute but only decomposed at the higher temperatures. An answer to this question might be obtained by using infrared spectroscopy with the sample in supercritical solution. However, carbon dioxide absorbs in the same spectral region as the isocyanate group[24], which would interfere with such a study.

Triisocyanates

Three triisocyanate samples were chromatographed at 100°C (Fig. 7), Desmodur R, Desmodur RF and Desmodur L. The peak on the tail of the solvent in Fig. 6A and B was probably phenyl isocyanate. When a concentrated solution of Desmodur R (*ca.* 20%) was injected, the two major peaks could still be distinguished, and were naturally overloaded. About 15 other peaks were also visible, which were probably various by-products. If the analysis cannot be performed at trace levels owing to problems with impurities or insufficient sensitivity, then a more concentrated injection solution will yield information about the minor sample components. However, injection of such concentrated samples could plug either the split or column restrictor.

Reaction of trimethylolpropane (TMP) with 2,4-TDI produces a carbamate triisocyanate which has lower volatility than diisocyanates. At 100°C, the analysis of such a sample, Desmodur L, resulted in the separation of two major and at least six

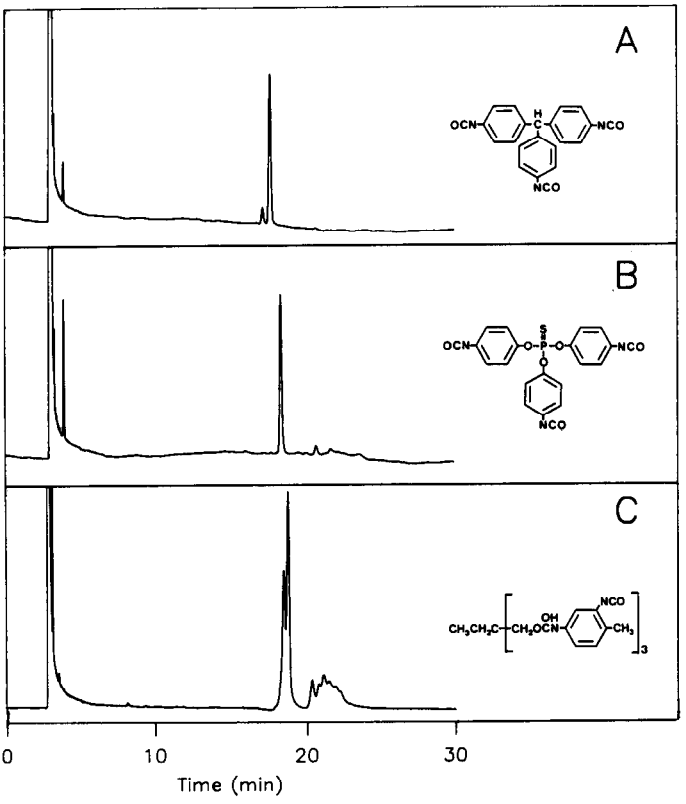


Fig. 7. CSFC traces of triisocyanate products. (A) Desmodur R: (B) Desmodur RF; (C) Desmodur L.

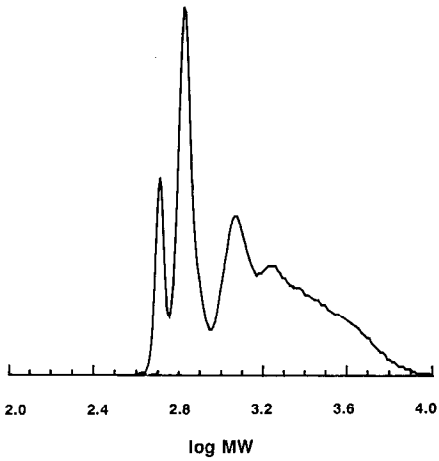


Fig. 8. GPC trace of the triisocyanate Desmodur L.

minor peaks (Fig. 7C). GPC analysis (Fig. 8) of Desmodur L indicated the presence of a component probably composed of TMP and two molecules TDI (referred to as the di-TDI adduct in the following discussion), the proposed product, a component with a molecular weight of about 1200 g mol^{-1}, and of some even higher molecular weight components. Comparison with the SFC trace indicated that the two closely eluting peaks at about 19 min are the di-TDI adduct and the proposed product, and the group of peaks at 20–23 min are the proposed product with additional substitutions, probably TDI. If the group of peaks at 20–23 min were the product then it would not be possible to explain the presence of six peaks in the group based on isomeric distribution, even considering the possible presence of both 2,4- and 2,6-TDI.

Urea and biuret isocyanates

Isocyanates can be converted into ureas, biurets and higher polyurets[16]. Most such derivatives are not amenable to analysis by GC owing to thermal lability. The chromatogram of an IPDI–urea adduct (H-2921) is shown in Fig. 9A. The sample contained about 40% IPDI[25]. The small peaks eluting at about 8 min were also present in the uncatalysed thiocarbamate reaction product discussed later (Fig. 14A). At least four peaks were separated at higher density in Fig. 9A. The major peak was assumed to be the urea. The relative peak area of the urea to IPDI was the same at 50 and 100°C, indicating no losses from the potential reaction of urea with free isocyanate. The IPDI–urea has a molecular weight of 400 g mol^{-1}. The small peaks eluting after the urea may be biuret adducts (*ca.* 642 g mol^{-1}), indicated by comparison with GPC results.

The substituted-biuret sample Desmodur N, formed from HDI, was chromatographed at 100°C (Fig. 9B). Tentative peak identifications were made by comparison with GPC results. A small amount of HDI was still present (peak 1), together with a significant amount of biuret. The proposed substituted-biuret structure, probably peak 4, has a molecular weight of 478 g mol^{-1}. The later eluting peaks (19.5–22

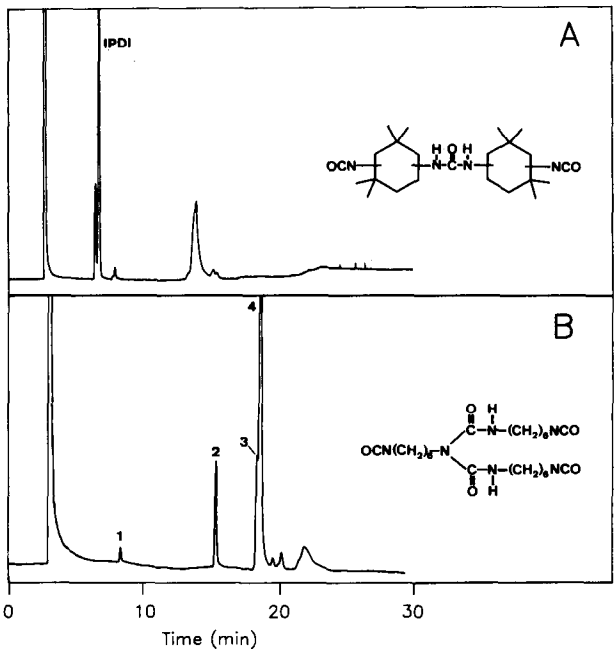


Fig. 9. CSFC traces of isocyanate–urea-derived products. (A) IPDI–urea, H-2921; (B) substituted biuret, Desmodur N. Peak numbers in (B): (1) HDI; (2) biuret; (3) unidentified; (4) probable substituted biuret.

min), presumably higher polyurets, would have molecular weights of 646, 814 and 982 g mol^{-1}, corresponding to the addition of one, two and three HDI molecules, respectively, to the substituted-biuret structure. The results from GPC analysis indicated the presence of the 982 g mol^{-1} of polyuret, which is probably the peak at 22 min. Peak 3 could not be identified. The sample was also chromatographed at 50°C. In that case, resolution was higher between the major peak (4) and the peak eluting immediately before it (3), but was poorer between the major peak and later eluting peaks.

Uretedinedione isocyanates (dimers)

The common name for a uretedinedione is a dimer. The uretedinedione structure is noted to decompose above 130–150°C[11]. The dimer of 2,4-TDI, Desmodur TT, was chromatographed at 100°C (Fig. 10A). A small impurity was present that eluted after the major peak. The sample was also chromatographed at 150 and 175°C. There was slight decomposition at 150°C and almost complete decomposition at 175°C.

Another sample, BF1540, was described as the dimer of IPDI with dimerization occurring on the primary isocyanate. Aliphatic isocyanates do not generally form dimers[9,16], although trimers can be formed. The sample was chromatographed at 50–100°C in case the aliphatic uretedinedione structure was less thermally stable than the corresponding aromatic dimer, but the relative peak areas remained constant. At 100°C (Fig. 10B), at least ten major peaks were present. There appeared to be two

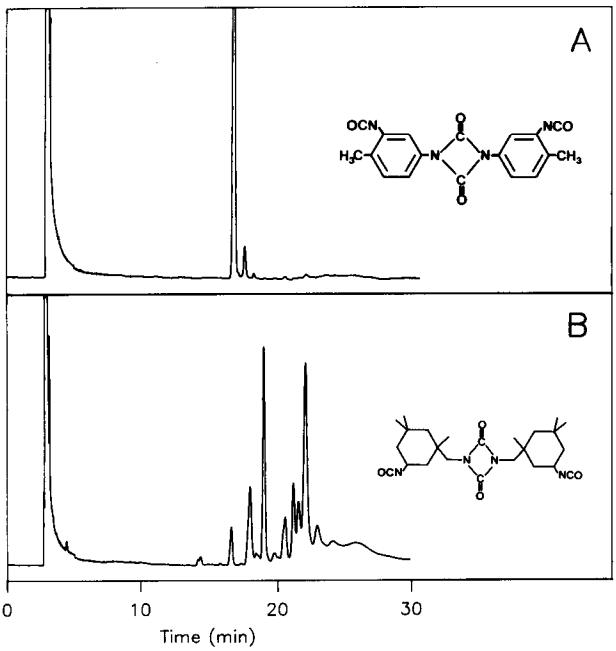


Fig. 10. CSFC traces of uretedinedione products of (A) 2,4-TDI, Desmodur TT; (B) IPDI, BF1540.

series of peaks, the first containing three major peaks of increasing concentration and the second 3–5 major peaks. There was also one very broad peak eluting at the higher density. The first series of peaks eluted with good profiles at the lower temperatures, but the latter peaks had very poor shape except when the temperature was 80°C or higher. The best results were obtained at 100°C. Although infrared spectroscopic analysis of BF1540 indicated the presence of the dimer group, there was very little free isocyanate, which indicated that the sample was highly polymerized. Comparison with GPC results indicated that components of up to 1500–2500 g mol^{-1} were eluted in CSFC. No definite peak identifications could be made.

Isocyanurate isocyanates (trimers)

The common name for an isocyanurate is a trimer; both aromatic and aliphatic isocyanates can form trimers[9,16]. The isocyanurate ring is the most thermally stable of the isocyanate-derived products included in this study. Polymer additives containing the isocyanurate ring have been chromatographed by CSFC at 140°C[26] and by high-temperature GC[27].

The trimer of IPDI, T1890/100, was chromatographed at 100°C (Fig. 11A). A series of five peak groups were present, which apparently constitute an homologous series. The first group contained three large and one small peak and the second group was barely separated into two peaks. These secondary series of peaks may arise from reactions of the primary and secondary isocyanate groups of IPDI, or from the *cis* and *trans* isomers. Comparison with GPC results (Fig. 12) indicated the largest group of peaks (15 min) was the trimer, and that the later eluting peaks corresponded to up

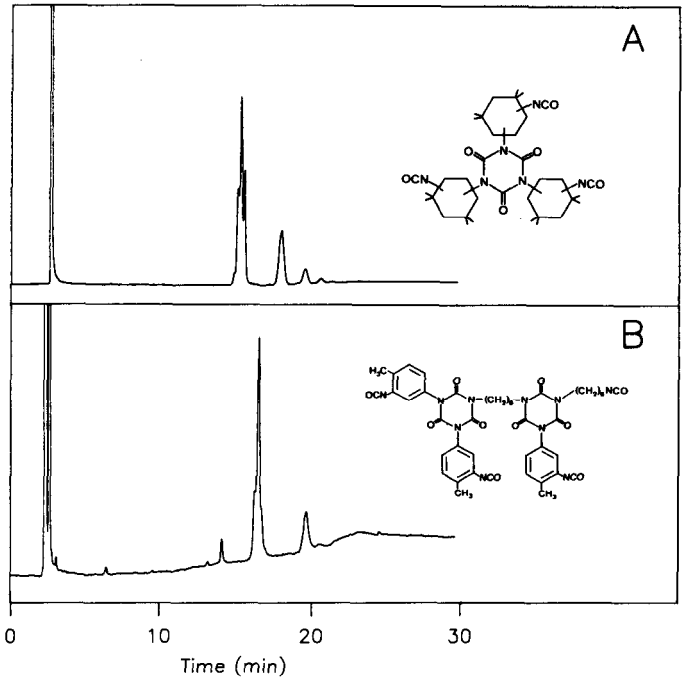


Fig. 11. CSFC traces of isocyanurate products. (A) IPDI–trimer, T1890/100; (B) Desmodur HL.

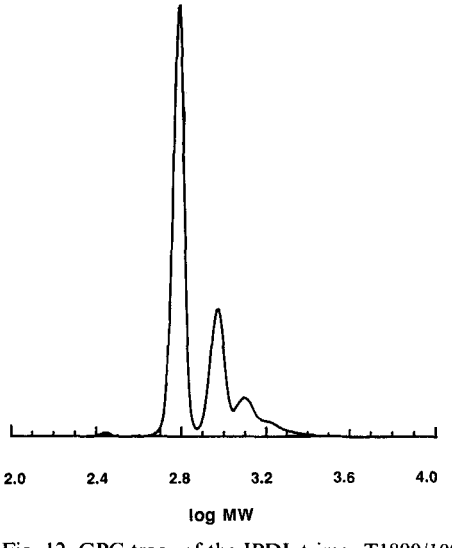


Fig. 12. GPC trace of the IPDI–trimer T1890/100.

to four additional IPDI molecules attached to the trimer. The highest molecular weight would be 1554 g mol^{-1}

One sample which is not a trimer but a high-molecular-weight polyisocyanate possessing two isocyanurate rings is Desmodur HL. The molecular weight of the proposed structure is 858 g mol^{-1} (Fig. 11B). CSFC analysis resulted in the elution of several peaks (Fig. 11B). A small amount of TDI and/or HDI was present (6 min). Three peaks at about 17 min were barely separated; these were probably combinations of TDI and HDI in a single isocyanurate ring (indicated by comparison with GPC). The peak at 20 min could be identified by comparison with results from GPC analysis as having a molecular weight close to the proposed structure. The molecular weight data from GPC analysis were not sufficiently precise to determine the exact structure of the eluted component.

Phenol-blocked isocyanate

A blocked isocyanate is one that has been reacted with any of a number of possible reagents, and that will decompose to the original products (isocyanate and blocking agent) on heat treatment. Phenol-blocked isocyanates will decompose to isocyanate and phenol at about 120°C[28], and are the most widely used. The trifunctional isocyanate Desmodur L (Fig. 7C) can be obtained as the phenol-blocked derivative, Desmodur AP, which was chromatographed at 100°C (Fig. 13). A single major peak was eluted, with a minor peak at higher density. Phenol was also present, eluting just after the solvent. The phenol was also detected when chromatographed at 50°C. Above 120°C, the major peak disappeared. No identifications could be made by comparison with results from GPC owing to dissimilar profiles.

Thiocarbamate adducts

Two different thiocarbamate products formed from the combination of IPDI and a mercaptosilane were chromatographed, one where a catalyst was used and one

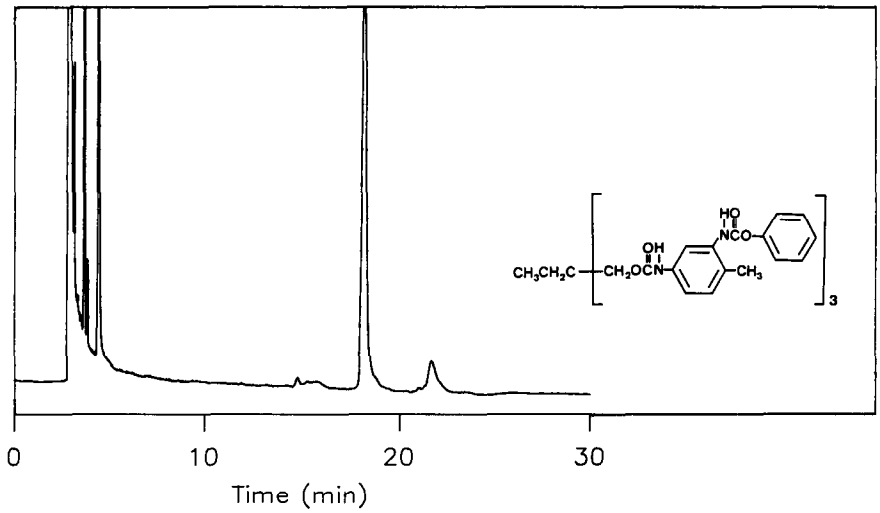


Fig. 13. CSFC traces of the phenol-blocked isocyanate product Desmodur AP.

without a catalyst (Fig. 14). Thiol–isocyanate reaction products are generally more thermally stable than the corresponding urethane adducts. In both samples the remaining IPDI was apparent, and in the uncatalysed product (Fig. 14A) a small amount of the thiol was still present. In the catalysed product (Fig. 14B) there were two major product peaks, but each appeared to be two peaks. This was indicated by the presence of a shoulder on the second product peak when chromatographed at 50°C. In the uncatalysed product (Fig. 14A) several other peaks were present in addition to the major product peaks. An apparently homologous series up to $n = 5$ or 6, possibly additional IPDI substitutions on the thiocarbamate, were eluted in this chromatogram. At higher sample concentration, oligomers up to $n = 8$ could be detected, of molecular weight nearly 2000 g mol^{-1}, determined by comparison with GPC results (Fig. 15).

The additional early eluting peaks, between 11 and 14 min, with the uncatalysed sample (Fig. 14A) could not be immediately identified. They were tentatively identified as the dimer or trimer of IPDI, or possibly ureas. None of these peaks corresponded to any of the peaks in the IPDI dimer sample BF1540 (Fig. 10B). The group of peaks at about 11 min was also present in a small amount in the IPDI–urea sample (Fig. 9A), but the urea was the later eluting peak in Fig. 9A. The retention patterns and relative peak areas between these unidentified peaks and the IPDI–trimer sample (Fig. 11A) were similar, but the elution densities were substantially different. No definitive peak identities could be made without confirmation by mass spectrometry. However, the most reasonable explanation is that the unidentified peaks in the uncatalysed sample were IPDI dimer, that the IPDI–urea and trimer structures (Fig. 9A and 11A) were as assumed and, hence, that the BF1540 sample (Fig. 10B) did not

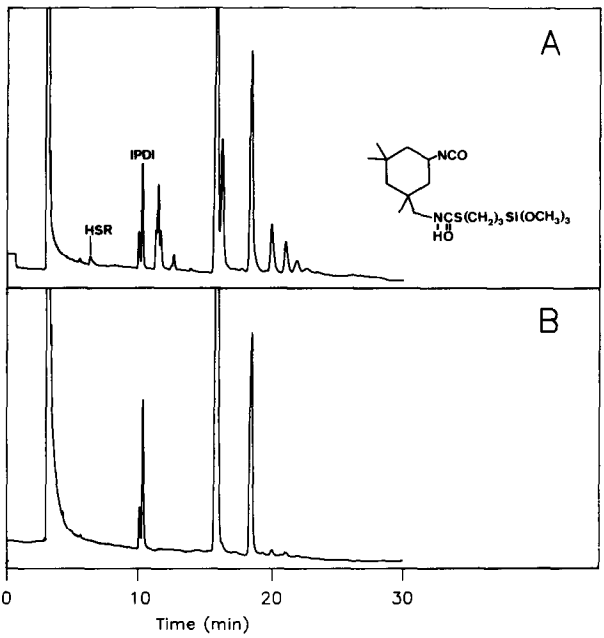


Fig. 14. CSFC traces of thiocarbamate adducts. (A) Uncatalysed and (B) catalysed reaction products.

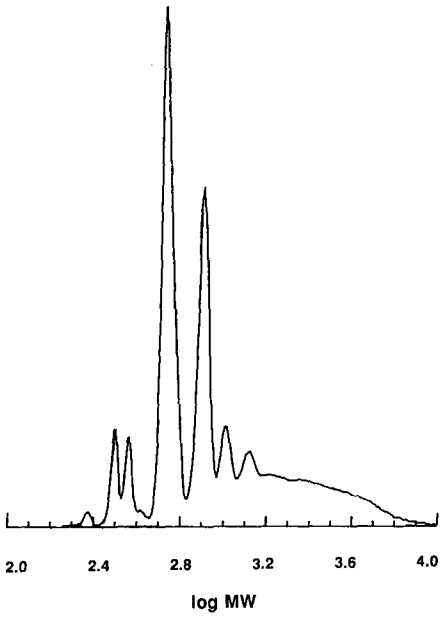


Fig. 15. GPC trace of thiocarbamate adduct (uncatalysed reaction product).

contain the dimer of IPDI. In addition to the IR data noted above, GPC analysis of the BF1540 sample also indicated that no dimer was present. This explanation would also correspond better to the general trend of higher elution density with higher molecular weight.

Gas chromatographic analysis

All samples were tested for compatibility with gas chromatography (GC) using cold, on-column injection and a non-polar stationary phase. Some of the low-molecular-weight diisocyanates have been analysed underivatized at trace levels[15,29], and all diisocyanates in this study eluted without decomposition. MDI has been demonstrated to be amenable to GC[30,31]. Whereas MDI eluted well in GC, higher oligomers did not elute in this study, although some injections produced peaks for the oligomer of $n = 1$. The Isonate 143L sample produced peaks for the MDI oligomer, but the major peak tailed severely and no other peaks were present, which would have corresponded to the carbodiimide. The triisocyanate Desmodur R could be eluted with good peak shape. All other samples decomposed during GC analysis.

GPC analysis

The GPC profiles of polymeric MDI products, thiocarbamate adducts, IPDI–trimer and IPDI–urea corresponded well with the CSFC results. This indicated that all or nearly all of each sample eluted with CSFC. For the samples Desmodur N, L and AP, it appeared that only 50–70% of the samples eluted with CSFC. For two samples, the IPDI–dimer BF1540 and Desmodur HL, it appeared that only about one third of the samples eluted with CSFC. The non-eluting fractions of these samples were represented in GPC by broad distributions of up to 10 000 g mol^{-1} or more.

Chromatographic degradation from highly polymerized isocyanates

With polymeric isocyanates or isocyanate–polyol prepolymers there may exist homologues of extremely high molecular weight, of 10 000 g mol^{-1} or more. Many lower molecular weight isocyanates will polymerize on standing. In CSFC it is always desirable to elute all of an injected sample. However, it is possible that only isocyanates up to certain molecular weights will elute with a given mobile phase. In this instance there will be a build-up of sample on the column, necessitating measures such as the use of precolumns or cutting off part of the column occasionally during extended, routine analyses. An undesirable situation would develop when other types of samples are injected on to the same column, such as alcohols. This could easily lead to polyurethane formation on the column, which would be detrimental to quantitation, consistency in selectivity and extended column lifetimes. No chromatographic degradation was observed in this study. A supercritical-fluid extraction–injection system which would transfer only those components of a sample that are soluble in the mobile phase to the column would be extremely valuable, both for these samples and for many other high-molecular-weight samples analysed by either packed or capillary column SFC. Alternatively, a different mobile phase, either mixed or neat, may elute the higher-molecular-weight isocyanates that cannot be eluted with carbon dioxide.

CONCLUSIONS

The results demonstrate that CSFC provides more information regarding sample composition than any other available chromatographic technique, especially for polymeric isocyanates, or where mixtures of isomeric and/or by-products are present. Further improvements in resolution can be obtained using longer (10–20 m) and smaller I.D. (50 μm) columns, and varying the programme types and parameters. The higher degree of polarizability of the isocyanates produced strong interactions with the biphenyl stationary phase. With several samples not all of the sample components eluted with a carbon dioxide mobile phase. With a neat carbon dioxide mobile phase the applicable mass range had an upper limit of 500–2000 g mol^{-1}, depending on sample structure and composition. The most reasonable estimates of peak identities were made on the basis of known or proposed structures, elution profiles and comparison with results from GPC. However, confirmation of peak identities will require analysis by SFC–mass spectrometry.

Operating temperatures of up to 100°C could be used with a carbon dioxide mobile phase when analyses were performed at a screening level. However, the possibility of temperature-catalysed reactions of isocyanates with themselves or impurities in either the sample or mobile phase cannot be excluded for all possible samples. The purity of the mobile phase will require additional study if trace analysis is to be performed with CSFC.

The successful separations demonstrated in this study indicate the range of isocyanate samples that are soluble in neat carbon dioxide. Although the insolubility of the highly polymerized sample fractions is detrimental to chromatographic analysis, these differences in solubility could be exploited in the development of fractionation and extraction processes. Samples of isocyanates, isolated from polymerized fractions, could yield a higher degree of control over isocyanate reactions.

REFERENCES

1 C. J. Purnell and R. F. Walker, *Analyst (London)*, 110 (1985) 893; and references cited therein.
2 M. Dalene, L. Mathiasson, G. Skarping, L. Sango and J. F. Sandstrom, *J. Chromatogr.*, 435 (1988) 469.
3 T. Alfredson, *Int. Lab.*, 11 (1981) 46.
4 D. W. Later, B. E. Richter, W. D. Felix, M. R. Andersen and D. E. Knowles, *Am. Lab.*, 18 (1986) 108.
5 J. Huau and C. Tinet, *Inf. Chim.*, No. 285 (1987) 151.
6 K. Grolimund, W. P. Jackson, M. Joppich, W. Nussbaum, K. Anton and H. M. Widmer, in D. Ishii, K. Jinno and P. Sandra (Editors), *Proceedings of the Seventh International Symposium on Capillary Chromatography, Gifu, Japan, May 11–14, 1986*, The University of Nagoya Press, Nagoya, 1986, p. 625.
7 G. Woods, *ICI Polyurethanes Book*, Wiley, New York, 1987.
8 D. H. Chadwick and T. H. Cleveland, in *Kirk–Othmer Encyclopedia of Chemical Technology*, Vol. 13, Wiley-Interscience, New York, 1981, p. 789.
9 J. H. Saunders and K. C. Frisch, *Polyurethanes, Chemistry and Technology, Part I, Chemistry*, Interscience, New York, 1962.
10 D.W. Later, Lee Scientific, personal communication.
11 C. Hepburn, *Polyurethane Elastomers*, Applied Science, Barking, 1982.
12 S. Ozaki, *Chem. Rev.*, 72 (1972) 457.
13 O. Stallman, *U.S. Pat.*, 2 671 082, 1954.
14 R. G. Arnold, J. A. Nelson and J. J. Verbanc, *Chem. Rev.*, 57 (1957) 47.
15 G. Skarping, B. E. F. Smith and M. Dalene, *J. Chromatogr.*, 331 (1985) 331.
16 H. J. Twitchett, *Chem. Soc. Rev.*, 3 (1974) 209.
17 J. C. Kuei, J. I. Shelton, L. W. Castle, R. C. Kong, J. S. Bradshaw and M. L. Lee. *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 13.
18 S. M. Fields and M. L. Lee, *J. Chromatogr.*, 349 (1985) 305.
19 D. W. Later, E. R. Campbell and B. E. Richter, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 11 (1988) 65.
20 S. M. Fields, *Ph.D. Dissertation*, Brigham Young University, Provo, UT, 1987.
21 T. W. Campbell and J. J. Monagelle, *J. Am. Chem. Soc.*, 84 (1962) 1493.
22 P. Fischer, *Br. Pat.*, 899 036 (1960).
23 H. Urlich, in *Encyclopedia of Polymer Science and Engineering*, Vol. 8, Wiley-Interscience, New York, 1987, p. 448.
24 P. Morin, M. Caude, H. Richard and R. Rosset, *Chromatographia*, 21 (1986) 523.
25 *Polyisocyanate IPDI H2921*, Product Bulletin, Hüls, Marl, F.R.G.
26 M. W. Raynor, K. D. Bartle, I. L. Davies, A. Williams, A. A . Clifford, J. M. Chalmers and B. W. Cook, *Anal Chem.*, 60 (1988) 427.
27 W. Blum and L. Damasceno, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 10 (1987) 472.
28 Z. W. Wicks, *Prog. Org. Coat.*, 3 (1975) 73.
29 G. Skarping, M. Dalene and L. Mathiasson, *J. Chromatogr.*, 435 (1988) 453.
30 I. Padovani and L. Trevison, *Chim. Ind. (Milan)*, 69 (1987) 30.
31 O. Suzuki and H. Brandenberger, *Fresenius Z. Anal Chem.*, 326 (1987) 228.