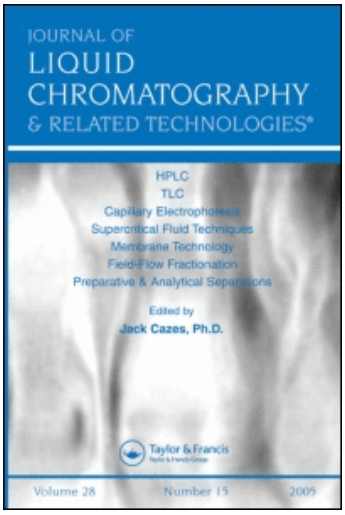

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EVALUATION OF 9-METHYLAMINO-METHYLANTHRACENE AS A CHEMICAL LABEL FOR TOTAL REACTIVE ISOCYANATE GROUP: APPLICATION TO ISOCYANATE OLIGOMERS, POLYURETHANE PRECURSORS, AND PHOSGENE

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ABSTRACT

9-Methylamino-methylanthracene (MAMA) is a secondary amine compound which can be used for derivatization and quantitation of isocyanate compounds by HPLC with detection by fluorescence and ultra-violet light absorbance. The compound has potential as a chemical label for determination of airborne total reactive isocyanate group (TRIG) compounds arising from partially polymerized polyurethanes and thermal decomposition products of fully cured polyurethanes. Six isocyanate oligomers and polyurethane precursors based on methylene-bis-(phenylisocyanate) (MDI), 1,6-hexamethylene-diisocyanate (HDI), and 2,4- and 2,6-toluenediisosocyanate (TDI) were assayed for isocyanate content using MAMA reagent. After reaction of isocyanate with MAMA, the urea derivatives were analyzed by reversed phase HPLC using three detection / quantitation modes: fluorescence with excitation at 245 nm and emission at 414 nm, UV absorbance at 245 nm and UV absorbance at 370 nm. The ratio of absorbance at 245 nm and at 370 nm identified multiple peaks originating from isocyanate-containing compounds in each sample. The total amount of TRIG in each sample was then quantitated by absorbance of these peaks at both of the UV wavelengths. For the test samples, observed recoveries of TRIG by MAMA-HPLC assay ranged from

96 to 105%, in comparison to a reference titration assay. The technique was also evaluated for chemical interference from phosgene gas. A single compound was found after reaction of MAMA with phosgene which responded as two equivalents of TRIG.

INTRODUCTION

The isocyanates are an important group of commercial chemicals used in the production of polyurethanes and of certain carbamate pesticides. These compounds are of particular interest in industrial hygiene due to their documented ability to act as respiratory irritants and skin and respiratory sensitizers.[1] The collection and measurement of specific airborne isocyanate monomers has become fairly routine using various secondary amine derivatizing agents with high performance liquid chromatographic determination. These compounds react with isocyanates to form substituted urea derivatives which can be detected by ultraviolet absorbance, fluorescence, or amperometry. Examples of some of these amine reagents include N-(n-propyl)-N-(4-nitrobenzyl)-amine,[2,3] methoxyphenyl-piperazine,[4] 1-(2-pyridyl)-piperazine,[5] 3-(2-aminoethyl)indole [tryptamine],[6] and 9-methylamino-methylanthracene [MAMA].[7]

Measurement of total reactive isocyanate group (TRIG) in air is of more recent interest. TRIG is comprised of any compound containing free isocyanate groups; this includes the monomeric diisocyanates commonly used in industry, as well as their oligomers which are becoming increasingly more popular due to their lower vapor pressures and consequently lower degree of hazard. In addition, TRIG includes any partially polymerized material containing free isocyanate such as would be found during the course of reaction between an isocyanate and a polyol to form a polyurethane.

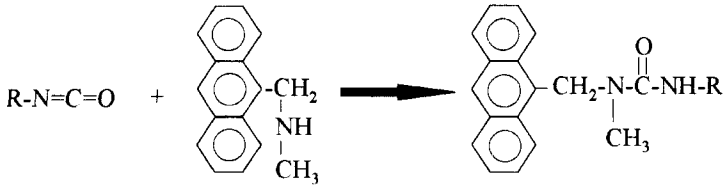
Essentially the only current working method for TRIG in air is that developed by the United Kingdom's Health and Safety Executive (HSE). HSE's

Method MDHS 25[8] uses a solution of methoxy-phenylpiperazine (MOPIP) in an impinger for collection of airborne TRIG. TRIG compounds react with the MOPIP to form urea derivatives which absorb in the ultraviolet region, are electrochemically active, and can be separated by HPLC. For a given diisocyanate monomer and its oligomers, a constant ratio between UV absorbance and electrochemical detector response is reportedly obtained.[4] Thus, a peak in the HPLC chromatogram is identified as an isocyanate compound, and the amount of TRIG is quantitated using the specific monomer as a standard. Total TRIG content of a sample is taken as the sum of the amounts of isocyanate equivalent for each of the identified TRIG peaks. The amount of isocyanate equivalent is determined from the electrochemical response of a given TRIG compound in comparison to standards made from the parent monomer compound.

The technique has had problems with specificity and the inability to deal with TRIG derived from more than one parent monomer.[9,10] In addition, TRIG compounds which are not simple oligomers of a given monomeric diisocyanate, such as might be found in polyurethane pyrolysis fumes, cannot be accurately quantified since they may have no direct relationship to the analytical response of the monomer standard. Additionally, recent work has shown that TRIG contained in partially polymerized urethanes made from toluene-diisocyanate (TDI) and ethylene glycol exhibited inconsistent ratios of response by electrochemical and UV absorbance detection as the number of polymer units increased.[11]

In the past, some work has been done on the determination of specific forms of TRIG using 9-(N-methylaminomethyl)-anthracene (MAMA) as the derivatizing agent. For example, the method was applied with some success to measure isocyanate monomer and oligomer in paint overspray.[12] Also, MAMA was used to determine TRIG in the emissions from thermal degradation of polyurethane binders.[13] More recently we have evaluated the potential of using MAMA as a chemical label for TRIG forms whose exact chemical structures are not known.[14] The basis of this application is the reaction of MAMA with

isocyanate groups to yield substituted urea derivatives which contain the anthracenyl moiety:



The anthracenyl group in MAMA is a highly specific chromogen and fluorogen which exhibits strong absorption at a primary wavelength of about 245 nm and shows a series of weaker absorption maxima between 350 and 400 nm.[7,14] The compound is also highly fluorescent, with an emission maximum at about 414 nm, and with major excitation maxima corresponding to the UV absorbance maxima.

In our previous work, the consistency of response by UV and fluorescence detection was evaluated in a series of urea derivatives prepared from MAMA and 11 isocyanate compounds.[14] Aliphatic, aromatic, mono- and di-isocyanates were included in order to evaluate possible structure / response relationships. The ratios of response factors (response factor = integrated area ÷ isocyanate concentration) for absorbance at 245 and 370 nm were relatively constant across isocyanates, with a mean of 10.46 and standard deviation of 0.87 (RSD = 8.3%). All eleven derivatives were also highly fluorescent, but they exhibited wide variability in response factors (RSD = 55%). The results suggested that the ratio of UV absorbance at 245 nm to that at 370 nm may be used for reliable identification of MAMA-derivatized TRIG, and that quantitation of MAMA-derivatized TRIG may be achieved with satisfactory accuracy using absorbance detection at either 245 or 370 nm.

The purpose of this work was to extend the evaluation of MAMA as a chemical label for TRIG by applying it to the assay of several oligomers and polyurethane precursors derived from three diisocyanate monomers: 1,6-hexamethylene diisocyanate (HDI), 2,4- and 2,6-toluenediisocyanate (2,4-TDI, 2,6-TDI), and 4,4'-methylene-bis-(phenylisocyanate) (MDI). These materials were first assayed for isocyanate content using a reference titrimetric procedure. They were subsequently derivatized with MAMA and analyzed by HPLC. The reliability of the method was further assessed by investigating potential interference from phosgene gas.

MATERIALS AND METHODS

9-Methylamino-methylanthracene was obtained from Aldrich Chemical Co. (Milwaukee, WI) in a purity of 99%. MDI (Rubinate 44®) was obtained from Rubicon Chemical Co. (Geismar, LA). HDI (98%) was obtained from Aldrich.

The following oligomeric isocyanate containing materials were evaluated in this study:

- **CMDI**, obtained from BASF Corp., Geismar, LA. This material nominally contains 58 - 68 % MDI monomer, with the remainder being oligomers of MDI.
- **Lupranate M20S**, obtained from BASF Corp., Geismar, LA. This material nominally contains 40% MDI monomer, and 60% MDI oligomers.
- **PMPPI [poly(methylene(polyphenylisocyanate))]**, obtained from Aldrich Chemical Co. This material is an oligomeric form of MDI.
- **Desmodur N100**, obtained from Mobay Corp., Baytown, TX. This is a homopolymer of HDI, with HDI-biuret (a trimer of HDI) being predominant. A maximum of 1.6% HDI monomer is expected after 3 to 6 months storage. The material was approximately 18 months in storage when used in this work.

- **Imron paint activator 192S**, manufactured by DuPont Automotive Products, Wilmington, DE. This material is a solution of about 33% HDI oligomers in butyl acetate, ethyl acetate, and trimethylbenzene.
- **Rexthane**, manufactured by the Sherwin-Williams Co., Cleveland, OH. This is a moisture-curing, heavy duty, polyurethane varnish containing 2,4- and 2,6-TDI monomers, polyurethane prepolymers (polyhydric alcohols modified with TDI), and xylene.

Reference Assay of Isocyanate Content

The isocyanate content of the study materials was determined using a standard titration procedure based on reaction of isocyanate with di-n-butylamine.[15] An aliquot of the test material (0.5 to 1 g) was weighed out and subsequently dissolved in 6 mL toluene previously dried over molecular sieve 5A. To the sample was added 2.0 N di-n-butylamine in toluene at a ratio of 7.5 mL to 1 gram of isocyanate-containing material. The sample was loosely capped and allowed to react for 15 minutes. Thirty-four mL of isopropanol were then added to the mixture, along with 75 μL bromocresol green indicator solution (0.1% in 0.02 N NaOH). The mixture was placed on a magnetic stirrer and the excess di-n-butylamine was titrated with standardized HCl solution, (~1.0 N). The isocyanate content of the test materials was calculated based on the number of equivalents of di-n-butylamine consumed during reaction in comparison to a reagent blank:

$$wt\%NCO = \frac{4.2N(B-S)}{W},$$

where N = normality of the HCl titrant,

B= volume of HCl required for titration of reagent blank,

S = volume of HCl required for titration of sample,

and W = mass of sample assayed.

Assay of Isocyanate Content by MAMA / HPLC

The MAMA-urea derivatives of MDI, 2,4-TDI, 2,6-TDI, and HDI were synthesized in the laboratory for use as analytical standards. The general procedure for synthesis of an isocyanate-MAMA-urea was as follows: to a solution of MAMA in hexane or hexane/methylene chloride was added the isocyanate compound, either neat or as a solution in hexane; the reaction was allowed to proceed with constant stirring during which the urea derivative precipitated out of solution; the urea precipitate was recovered by filtration and dried; the crude derivative was then recrystallized from a suitable solvent. A two- to five-fold excess of MAMA was used in these procedures. Reaction rates for the aromatic isocyanates were very rapid, with most reactions going to completion within 30 minutes. The aliphatic isocyanate, HDI, reacted slower, with several hours allowed to ensure completion of reaction.

Reaction of the isocyanate containing materials with MAMA reagent was carried out in a similar fashion: a known mass of polymeric isocyanate (0.1- 0.3 grams) was weighed out and dissolved in an appropriate solvent (dioxane for the MDI-based materials, 50/50 dioxane/dimethylformamide for Imron 192S, and dimethylsulfoxide for Desmodur N100 and Rexthane). The expected number of moles of isocyanate present were calculated based on the reference assay. The samples were then reacted with a 3 to 5 fold excess of MAMA, based on a stoichiometric reaction of one mole of MAMA with one mole of isocyanate group. The MAMA reagent was dissolved in the same solvent as the isocyanate-containing material prior to its addition.

Assessment of Interference from Phosgene

Phosgene was evaluated as a possible interferant for the method. Phosgene gas was generated from a permeation device (VICI Metronics, Santa Clara, CA) housed in a standards generator (AID Model 360, Avondale, PA) held at a

constant 30°C with a flow of 1.0 L/min of house air dried over silica gel. The output of the standards generator was further diluted with dried house air to yield a final test concentration of 100 ppb phosgene. To evaluate the potential interference, samples from this test atmosphere were collected in midget impingers containing 10 mL of a solution of 0.1 mg MAMA / mL in acetonitrile at a flow rate of 1.0 L/min for 30 minutes. These samples were then analyzed by the same HPLC-UV-fluorescence technique that was applied to the TRIG compounds. For this procedure, HDI-MAMA-urea was used as the standard reference material.

High Performance Liquid Chromatography

Chromatographic analysis of the MAMA-derivatized samples and standards was performed with a Perkin Elmer Model 410 high pressure liquid chromatograph fitted with a Rheodyne injection valve. Peak detection was accomplished by fluorescence using a Shimadzu Model RF551 fluorometric detector with excitation at 245 nm and emission at 414 nm, and by ultraviolet absorption at two wavelengths using a Perkin Elmer Model LC90 UV detector set at a wavelength of 245 nm and a Waters Model 450 UV detector set at a wavelength of 370 nm.

Sample injection volumes were defined by a 20-μL sample loop. Samples were analyzed on a Supelcosil LC-8-DB octyl bonded phase column, 5 μm particle size (Supelco, Belafonte, PA). The column dimensions were 4.6 mm i.d. by 5 cm long. The mobile phase consisted of a mixture of acetonitrile and aqueous triethylammonium phosphate buffer (3% triethylamine in water, adjusted to pH 3.0 with phosphoric acid). The acetonitrile concentration was adjusted to ensure chromatographic separation of excess MAMA reagent and the individual isocyanate containing compounds in the samples, while minimizing chromatographic run times for the late eluting compounds. A concentration of 60% acetonitrile in the mobile phase at a flow rate of 1 mL/min was utilized for the

HDI-based samples, for analysis of the Rexthane sample, a mobile phase containing 54% acetonitrile was used at an initial flow rate of 2 mL/min which was increased to 4 mL/min after the elution of the TDI monomers. For the MDI-based materials, a mobile phase containing 60% acetonitrile was used at an initial flow rate of 1 mL/min for 22 minutes to allow elution of the MDI monomer and one oligomer, and then was increased to 2 mL/min. For those cases where the mobile phase flow rate was increased during a chromatography run, the measured areas of peaks of interest were corrected for the proportional change in integrated detector response due to the resulting reduction in residence times in the detectors.

All chromatograms were recorded and integrated using EZ CHROM software with data collection by a Strawberry Tree I/O board. Chromatograms were screened for presence of TRIG-derived peaks by comparison to the respective isocyanate parent monomer standard. The criteria for classification of a peak as being of TRIG origin was a detector response ratio for UV absorbance at 245 nm to that at 370 nm within ± 20% of that for the monomer standard. The 20%-criteria was derived as an approximation of the 95% confidence interval of the overall mean response observed in our previous work which applied the MAMA technique to eleven different isocyanate monomers.[14] Further confirmation of the identity of an unknown TRIG containing compound was provided by examination of its fluorescence response. In general, the flourescence of the identified TRIG compounds was of the same order of magnitude as their corresponding diisocyanate monomer standards, although there appeared to be a general trend of decreasing flourescence with increasing chromatographic retention time.

After identification of a TRIG compound, the amount of isocyanate present was determined in comparison to the response of the parent monomer standard. This was done for each of the UV absorbance detectors independently. Calibration of detector response for quantitation of TRIG in these compounds used conversion factors based on two moles TRIG / mole of diisocyanate monomer standard; i.e., for MDI, 0.121 μg TRIG / μg MDI-MAMA-urea; for HDI, 0.138 μg TRIG / μg

HDI-MAMA-urea; and for 2,4- and 2,6-TDI, 0.136 μg TRIG / μg TDI-MAMA-urea. In order to quantitate TRIG in the Rexthane sample, an average calibration curve was generated by combining the data for the 2,4- and 2,6-TDI standards and performing a linear regression of detector response vs. concentration with equal weighting for the responses of 2,4-TDI and 2,6-TDI.

RESULTS & DISCUSSION

Assay of TRIG Content of Test Samples

Figures 1 through 3 present representative chromatograms from each of the three classes of oligomeric isocyanates. In each case, excess MAMA reagent elutes at the beginning of the chromatogram, with MAMA-derivatized isocyanate-containing compounds, including that from the respective parent monomers, eluting later. In each case, baseline separation of excess MAMA from other constituents in the samples is obtained. The parent isocyanate monomers are the first eluting compounds of interest in each sample. Later eluting compounds are presumably either oligomers of the parent monomer isocyanate or polyurethane prepolymers formed by reaction of isocyanate with polyols or water. The elution order of these compounds is expected to be greatly influenced by molecular weight, with longer chain oligomers eluting later in the chromatographic run.

All three of the MDI-based materials contain significant amounts of MDI monomer, identified as peak number 1 in the chromatogram of the CMDI sample (Figure 1) and in Table I, which presents the results of the assays of each of the test materials. CMDI contains MDI monomer as well as two other peaks identified as isocyanate compounds. The third peak appears to actually be two unresolved compounds which are co-eluting. However, this does not interfere with the goal of assaying this sample for TRIG, and quantitating the contribution

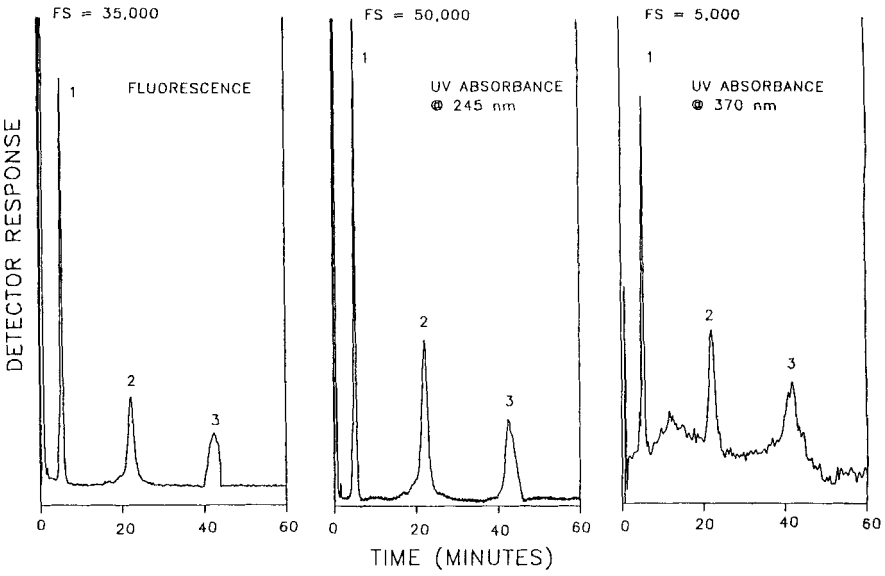


FIGURE 1 Chromatogram of a sample of CMDI containing 100 μmole TRIG per L. Chromatographic conditions: Supelcosil LC-8-DB column, 4.6 mm x 5 cm; 60% acetonitrile / 40% aqueous triethylammonium phosphate buffer; 1 mL/min for 22 minutes, then increased to 2 mL/min. Numbered peaks are TRIG containing compounds identified by ratio of response of UV detectors.

of these compounds to the total isocyanate content of the sample of CMDI is straightforward. In the other MDI-based samples, the monomer and only one other compound in the chromatogram are identified as containing isocyanate. PMPPI and M20S display very similar composition, suggesting these materials may actually be the same formulation distributed under different product names.

There is a high degree of consistency in the ratio of detector responses used to identify TRIG compounds in the three MDI-based materials. MDI monomer standard shows a detector response ratio of 9.9 for UV absorbance at 245 nm and 370 nm. The observed response ratios of the TRIG compounds identified in the MDI-based materials range from 9.6 to 10.5 (97% to 106% of the MDI standard).

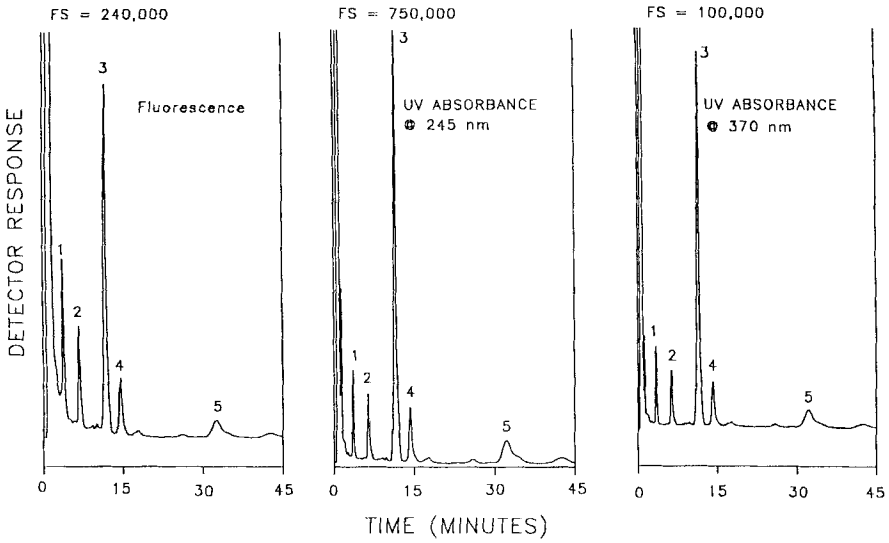


FIGURE 2 Chromatogram of a sample of Desmodur N100, containing 98.7 μmole TRIG per L. Chromatographic conditions: Supelcosil LC-8-DB column, 4.6 mm x 5 cm; 60% acetonitrile / 30% aqueous triethylammonium phosphate buffer, 1 mL/min. Numbered peaks are TRIG containing compounds identified by ratio of response of UV detectors.

Quantitation of total TRIG in the MDI-based samples using the MDI-MAMA-urea standard at either UV wavelength produces results that are not statistically different in comparison to the reference titration assay. For the M20S sample, a recovery of 105% is seen for quantitation at 245 nm in comparison to the reference assay for TRIG; for quantitation at 370 nm, 99% recovery is observed. For the CMDI sample - which includes the unresolved compounds identified as peak 3 - the respective recoveries are 105% and 104%, for the sample of PMPPI, recoveries of 95% and 96%, respectively, are obtained.

The data for the HDI-based materials is shown in Table II, while Figure 2 presents a chromatogram of the Desmodur N100 sample. In this chromatogram, four peaks are identified as having contained isocyanate. Peak 1 is HDI monomer

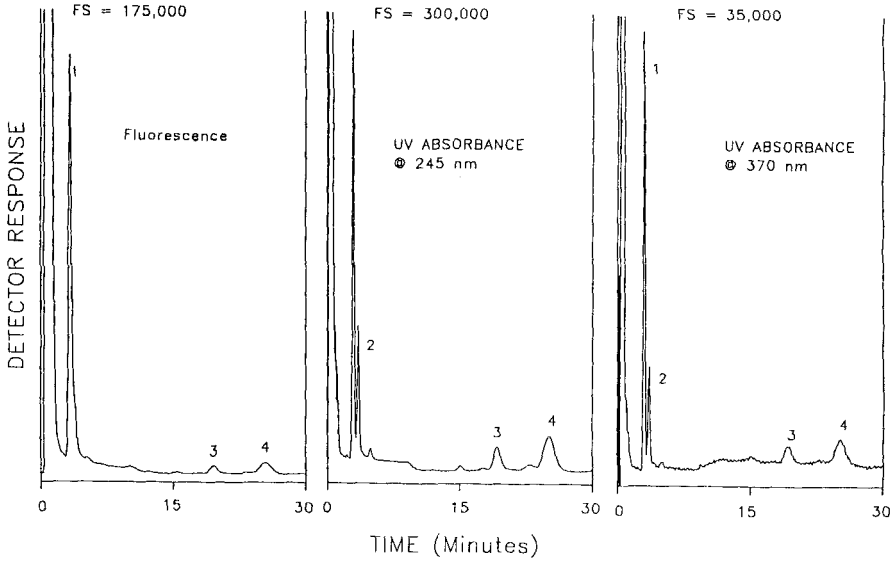


FIGURE 3 Chromatogram of a sample of Rexthane, containing 127 µmole TRIG per L. Chromatographic conditions: Supelcosil LC-8-DB column, 4.6 mm x 5 cm; 54% acetonitrile / 46% aqueous triethylammonium phosphate buffer, at 2 mL/min initially, increased to 4 mL/min. Numbered peaks are TRIG containing compounds identified by ratio of response of UV detectors.

TABLE I
MAMA Assay of TRIG Content of MDI-Based Samples

Material	Peak No.	Detector Response Ratio (245 nm: 370 nm)	weight % TRIG		
			MAMA (245 nm)	MAMA (370 nm)	Reference Assay*
MDI monomer standard	1	9.9 ± 3.0%	---	---	---
M20S	1	9.9 ± 10.0%	18.1 ± 8.9%	17.2 ± 6.4%	---
	2	10.5 ± 2.9%	4.9 ± 1.8%	4.5 ± 4.9%	---
	total	---	23.0 ± 6.7%	21.6 ± 4.7%	21.9 ± 10.5%
CMDI	1	9.6 ± 2.1%	7.2 ± 2.9%	7.2 ± 4.2%	---
	2	9.9 ± 2.0%	6.3 ± 4.4%	6.2 ± 3.7%	---
	3	9.7 ± 2.1%	10.6 ± 4.1%	10.6 ± 5.9%	---
	total	---	24.1 ± 3.0%	23.9 ± 3.9%	23.0 ± 1.7%
PMPPI	1	9.7 ± 3.1%	16.3 ± 5.0%	16.4 ± 7.3%	---
	2	9.6 ± 2.1%	5.7 ± 1.6%	5.8 ± 2.0%	---
	total	---	22.0 ± 3.6%	22.1 ± 5.3%	23.1 ± 5.6%

* reference assay by titration with di-n-butylamine / HCl
N.B.: all values are mean ± coefficient of variation

TABLE II
MAMA Assay of TRIG Content of HDI-Based Samples

Material	Peak No.	Detector Response Ratio (245 nm: 370 nm)	weight % TRIG		
			MAMA (245 nm)	MAMA (370 nm)	Reference Assay*
HDI monomer standard	1	8.3 ± 2.4%	---	---	---
Desmodur N100	1	8.7 ± 8.0%	0.7 ± 10.2%	0.7 ± 3.0%	---
	2	8.9 ± 3.4%	0.7 ± 1.0%	0.7 ± 2.5%	---
	3	8.4 ± 0%	11.5 ± 2.5%	11.3 ± 2.4%	---
	4	9.3 ± 3.2%	1.8 ± 2.4%	1.6 ± 2.7%	---
	5	15.5 ± 5.0%	0	0	---
	total	---	14.7 ● 2.5%	14.3 ± 4.4%	14.0 ± 10.0%
Imron 192S	1	none detected	---	---	---
	2	none detected			
	3	9.0 ± 5.6%	4.7 ± 1.9%	4.3 ± 6.3%	---
	4	8.9 ± 5.6%	0.6 ± 6.6%	0.6 ± 8.9%	---
	total	---	5.3 ± 1.7%	4.8 ± 5.8%	5.0 ± 2.6%

* reference assay by titration with di-n-butylamine / HCl
N.B.: all values are mean ± coefficient of variation

and accounts for less than 5% of the total TRIG in this sample. In contrast, no HDI monomer is detected in the sample of Imron 192S. Peak 3 is presumed to be HDI-biuret since it is clearly the largest component of both samples. Peaks 2 and 4 are TRIG-containing compounds of unknown structure which are presumably other oligomeric forms of HDI. Peak 5 in the chromatogram is not considered to have contained isocyanate since its detector response ratio is 15.5, which is outside of the selection criteria. The detector response ratios of the four TRIG compounds identified in these samples range from 8.4 to 9.3, equivalent to a range of 101 to 112% of that of the HDI-monomer standard which has an average detector response ratio of 8.3.

Quantitation of total TRIG in the HDI-based samples yields results that are not significantly different from that of the reference titration assay. For the Desmodur N100 sample, recoveries of 105% and 102% are obtained when quantitating TRIG by UV absorbance at 245 nm and 370 nm, respectively. For Imron 192S, these recoveries are 106% and 96%, respectively.

The Rexthane sample contains both 2,4-TDI and 2,6-TDI monomers as well as two other late-eluting compounds that contain isocyanate according to the selection criteria (Figure 3 and Table III). The detector response ratios of these two peaks are 11.8 and 12.7, respectively; whereas the monomer standards exhibit ratios of 9.8 and 10.9 (2,6-TDI and 2,4-TDI, respectively). The response ratios of the two unknown peaks are within the selection criteria of ± 20% when compared to 2,4-TDI. However, peak 4 is outside of the selection criteria when compared to 2,6-TDI (130% of the ratio for 2,6-TDI). It should be noted that the two TDI monomers - which are clearly identified in the Rexthane sample by retention time, UV absorbance, and fluorescence - also exhibit detector response ratios that are slightly higher than expected (10.5 and 12.6, respectively). This is felt to be a result of a shift in instrument performance between the times of analysis of the standards and the samples.

Quantitation of TRIG in the Rexthane sample yields recoveries of 107% and 100% for UV absorbance at 245 nm and 370 nm, respectively, in comparison to the titration assay. The contribution of TRIG in this sample from the two TDI monomers amounts to approximately 55% of the total. 2,6-TDI accounts for about three times as much TRIG as 2,4-TDI. This is in line with previously published data showing that in partially reacted polyurethane systems, free 2,6-TDI predominates over free 2,4-TDI.[3] This occurs in spite of the fact that typical commercial grades of TDI range from 80% to 65% 2,4-TDI. This phenomenon is a result of the much greater reactivity of 2,4-TDI in comparison to that of 2,6-TDI, with steric hindrance in the latter reducing its relative reactivity.

Overall, TRIG containing compounds in these six samples are readily identified by the screening criteria of UV absorbance detector response ratio.

TABLE III
MAMA Assay of TRIG Content of a TDI-Based Sample

Material	Peak No.	Detector Response Ratio (245 nm: 370 nm)	weight % TRIG		
			MAMA (245 nm)	MAMA (370 nm)	Reference Assay*
2,6-TDI monomer standard	1	9.8 ± 6.1%	---	---	---
2,4-TDI monomer standard	2	10.9 ± 4.6%	---	---	---
Rexthane	1	10.5 ± 1.9%	0.7 ± 4.4%	0.7 ± 5.0%	---
	2	12.6 ± 9.5%	0.2 ± 5.2%	0.2 ± 7.7%	---
	3	11.8 ± 10.2%	0.3 ± 9.4%	0.3 ± 15.9%	---
	4	12.7 ± 6.3%	0.5 ± 7.8%	0.5 ± 16.1%	
	total	---	1.7 ± 7.5%	1.6 ± 5.9%	1.6 ± 1.9%

* reference assay by titration with di-n-butylamine / HCl
N.B. all values are mean ± coefficient of variation

Additional confirmation is provided by fluorescence response. In line with our previous work on isocyanate monomers,[14] there appears to be a trend of enhanced UV absorbance response associated with the presence of aromatic structures and urea linkages in these compounds. This is especially reflected in the observed detector ratios since absorbance at 245 nm is likely to be significantly enhanced by these chemical structures, whereas absorbance at 370 nm would be minimally influenced. Quantitation of total TRIG by absorbance at 370 nm also appears to be slightly more accurate than that at 245 nm because of this effect. However the increased specificity at 370 nm comes at a significant loss in sensitivity - the response factors for absorbance at 245 nm being greater by approximately a factor of ten.

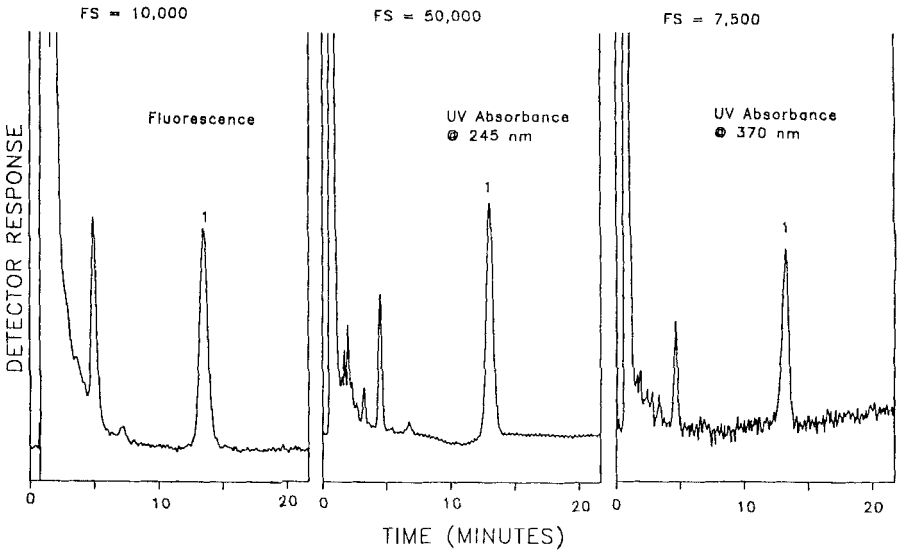
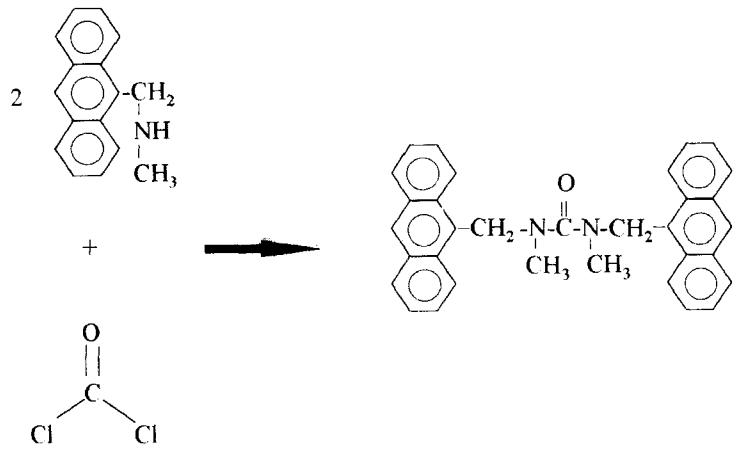


FIGURE 4 Chromatogram of a sample of MAMA reagent in acetonitrile reacted with phosgene gas. Chromatographic conditions: Supelcosil LC-8-DB column, 4.6 mm x 5 cm; 56% acetonitrile / 44% aqueous triethylammonium phosphate buffer, 1 mL/min. Peak 1 is a reaction product which responds as two equivalents of isocyanate group.

Interference from Phosgene

A chromatogram showing the result of reacting MAMA reagent with phosgene gas is shown in Figure 4. A peak with a retention time approximately twice that of HDI-MAMA-urea (13 minutes in comparison to 6.5 minutes for HDI-MAMA-urea) is apparent. In addition to being fluorescent, this compound exhibits a UV absorbance detector ratio of 10.5 ± 0.9 which is within 1% of that for the HDI standards used for comparison. Peak 1 in the chromatogram therefore falls within the criteria for classification as an apparent source of TRIG. The other unmarked peaks in the chromatogram are also present in the reagent blank and represent excess MAMA reagent and unknown contaminants.

The reaction of phosgene with secondary amine reagents used for derivatizing isocyanate compounds is well recognized[15] and may occur with all of these reagents. In the case of MAMA reagent, the expected reaction with phosgene would be as follows:



In this experiment, the equivalent response of 100 ppb phosgene in comparison to HDI-MAMA-urea standards is found to be 239 ± 15 ppb TRIG. In line with the reaction scheme illustrated above, phosgene appears to react with MAMA as two TRIG equivalents. Thus phosgene presents a potentially significant positive interference in the determination of TRIG using the MAMA reagent and HPLC-UV technique. Furthermore, the occurrence of phosgene and isocyanates together is likely in the manufacturing process since isocyanates are commonly synthesized by reacting phosgene with the corresponding amine. However, in the isocyanate application industries, such as polyurethane painting and flexible and rigid foaming, as well as in reformulating operations where paint and other surface coatings are manufactured, it is unlikely that phosgene would be present in significant amounts. Further, when the presence of phosgene is

suspected in a sample, it could be easily identified by chromatographic retention time and either analyzed separately or not included in the calculation of TRIG content. Triphosgene has been shown to be an acceptable surrogate standard for phosgene analysis using pyridyl-piperazine, one of the common secondary amine reagents used for isocyanate analysis.[15] It is likely that triphosgene would be an acceptable substitute standard for phosgene when using the MAMA reagent system for TRIG analyses.

CONCLUSIONS

The purpose of this work was to further illustrate the use of MAMA reagent as a chemical label for identification and quantitation of TRIG. Previous work indicated that for MAMA-derivatized isocyanates, the ratio of response of UV absorbance at 245 and 370 nm was relatively constant regardless of the structure of the isocyanate parent material.[14] Coupled with the intense fluorescence of TRIG-MAMA derivatives, this UV-absorbance screening technique proved to be a powerful approach to discriminating unknown TRIG forms from other materials in real samples. In the current work, the method was applied to the assay of six isocyanate containing materials which were based on MDI, HDI, or TDI. These materials ranged from industrial formulations of oligomeric isocyanates to two-component and moisture-curing polyurethane surface coatings. TRIG compounds in these samples were easily identified by HPLC with detection by UV absorbance and fluorescence. Quantitation in comparison to the parent diisocyanate monomer yielded quantitative recoveries of TRIG content as compared to a reference titration procedure. A significant interfering peak from reaction of MAMA with phosgene gas was identified but should be easily corrected after chromatographic separation from the rest of the sample. Overall this method appears to be superior to the MOPIP derivatization

procedure for TRIG which uses HPLC with UV and electrochemical detection. As part of ongoing evaluations of the MAMA technique, we are currently using the method to investigate the nature and behavior of TRIG compounds in laboratory test atmospheres and in actual workplace environments.

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