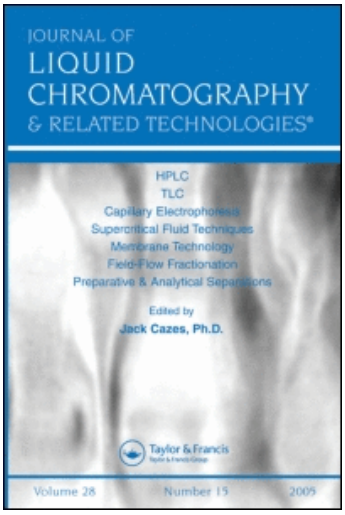

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EVALUATION OF 9-METHYLAMINO-METHYLANTHRACENE AS A CHEMICAL LABEL FOR TOTAL REACTIVE ISOCYANATE GROUP: A COMPARISON OF MONO- AND DI-ISOCYANATE MONOMERS

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ABSTRACT

9-Methylamino-methylanthracene (MAMA) is a secondary amine compound commonly used for derivatization and quantitation of specific commercial isocyanate compounds by HPLC with detection by fluorescence and ultra-violet light absorbance. The determination of airborne total reactive isocyanate group (TRIG) compounds arising from partially polymerized polyurethanes and thermal decomposition products of fully cured polyurethanes is of interest in industrial hygiene. The potential application of MAMA to the measurement of TRIG has been evaluated using a series of 11 model isocyanate compounds, including aliphatic and aromatic, mono-, and di-isocyanates. After synthesis, purification, and characterization, the 11 isocyanate-MAMA urea derivatives were analyzed by reversed phase HPLC using three detection / quantitation modes: fluorescence with excitation at 245 nm and emission at 414 nm, and UV absorbance at 245 and 370 nm. ANOVA of the observed response factors showed statistically significant differences among the isocyanates for each of the detection modes. The most variable was fluorescence with an overall coefficient of variation of 55%, whereas absorbance at 245 nm and at 370 nm showed coefficients of variation of only 14% and 8.6%, respectively. The

ratios of response factors for absorbance at 245 nm and at 370 nm were relatively constant across isocyanates, with a mean of 10.46 and standard deviation of 0.87 (8.3%). Certain structure / response relationships were observed, particularly the enhancement of UV absorbance by aromatic isocyanate derivatives and a general decrease in fluorescence by derivatives containing unhindered aromatic rings conjugated to the urea group. These results suggest that the ratio of UV absorbance at 245 nm to that at 370 nm may be used for reliable *identification* of unknown MAMA-derivatized TRIG and that *quantitation* of MAMA-derivatized TRIG may be achieved with satisfactory accuracy using absorbance detection at 370 nm.

INTRODUCTION

The isocyanates are an important group of commercial chemicals used in the production of polyurethanes and of certain carbamate pesticides. In general, exposure to low levels of these chemicals can result in respiratory irritation. More importantly, several of the commercial monomeric diisocyanates are documented sensitizers, causing occupational asthma and possibly hypersensitivity pneumonitis with chronic workplace exposure.[1]

An area of increasing concern is the environmental behavior and potential health effects of total reactive isocyanate group (TRIG). TRIG essentially represents all free isocyanate chemical groups present in the work environment, whether due to mono-, di-, or poly-isocyanate compounds, and including the parent monomeric diisocyanate compounds common in industry.

TRIG compounds may be emitted into the workplace atmosphere from a variety of potential sources: (1) as unreacted monomeric diisocyanate (*e.g.*, 2,4- and 2,6-toluenediisocyanate, 4,4'-diphenylmethane-diisocyanate, 1,6-diisocyanatohexane) offgassing from production lines, spills, etc.; (2) as unreacted oligomeric isocyanate compounds mechanically introduced into the atmosphere from spray application of polyurethane coatings and foams, *e.g.*, HDI-biuret and polymethylene-polyphenyl-isocyanate; (3) as partially reacted isocyanate compound being emitted from industrial products, or being formed from reaction of oligo-isocyanates with water vapor, ammonia, or other

airborne chemicals containing labile hydrogen; and (4) as mixtures of vapor and aerosol isocyanate compounds produced from the thermal degradation of isocyanate based products, principally polyurethane plastics and coatings.

Currently, the Health and Safety Executive (HSE) of the United Kingdom has the only explicit standard regarding TRIG. Their approach has been to assume that the isocyanate (NCO) functional group is inherently responsible for observed health problems associated with exposure, regardless of the organic moiety to which the isocyanate group is attached. Thus, the allowable exposure level is 20 μg NCO per m^3 of air, which is simply based on an extrapolation of the equivalent TRIG level for 2,4-TDI, the standard for TDI being 40 $\mu g/m^3$, and there being 0.48 μg TRIG per μg TDI.

The collection and measurement of 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 as illustrated below:

$$R\text{-}N{=}C{=}O \; + \; H\text{-}NR'R'' \; \text{--------}> \; R\text{-}NH\text{-}CO\text{-}NR'R''$$

Examples of some of the amine reagents used 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]

The determination of total reactive isocyanate group (TRIG) in air is more problematic than quantitation of a known monomeric isocyanate compound. Several methods have been developed for determination of TRIG, all of which employ adaptations of working methods for monomeric diisocyanates.[8,9] In general, the approach is to use an amine derivatizing agent as a chemical label for the isocyanate group. The chemical moiety attached to the original amine compound is selectively detected during chromatographic analysis and the detector response is then proportional to the

amount of label present and thus isocyanate content. The non-specificity of HPLC detection techniques usually requires the use of at least two independent detectors operating in series. The ratio of the detectors is then used as the criteria for rejection or acceptance of an unknown peak as containing isocyanate.

The purpose of this work was to evaluate the potential of using MAMA as a chemical label for isocyanate. The MAMA group is a highly specific chromogen and fluorogen exhibiting strong absorption at a primary wavelength of about 245 nm and showing a series of weaker absorption maxima between 350 and 400 nm.[7] The compound is highly fluorescent, with an emission maximum at about 414 nm, with major excitation maxima corresponding to the absorbance maxima.

In this 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. Aliphatic, aromatic, mono- and diisocyanates were included in order to evaluate possible structure / response relationships. The specific isocyanates studied were as follows: methylisocyanate (MIC), butylisocyanate (BUT), phenylisocyanate (PIC), benzylisocyanate (BENZ), o- and p-tolylisocyanate (OTOL, PTOL), 1,6-hexamethylenediisocyanate (HDI), 4,4'-dicyclohexylmethane-diisocyanate (HMDI), 2,4- and 2,6-toluenediisocyanate (2,4-TDI; 2,6-TDI), and 4,4'-diphenylmethane-diisocyanate (MDI).

MATERIALS AND METHODS

9-Methylamino-methylanthracene was obtained from Aldrich Chemical Co. (Milwaukee, WI) in a purity of 99%. HMDI was supplied as the commercial product (Mondur W®) by Mobay Chemical Co. (Baytown, TX). MDI (Rubinate 44®) was obtained from Rubicon Chemical Co. (Geismar, LA).

MIC, BUT (98%), PIC (98+%), BENZ (99%), OTOL (99+%), PTOL (99%), HDI (98%), and 2,6-TDI (97%) were obtained from Aldrich. 2,4-TDI (98+%) was obtained from Fluka Chemicals (Ronkonkoma, NY).

Preparation of Isocyanate-MAMA Urea Derivatives

The general procedure for synthesis of a MAMA-isocyanate-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 and the reactions were usually complete in 30 minutes. The aliphatic isocyanates reacted slower and several hours were usually allowed for completion.

The identities of the purified derivatives were confirmed by elemental analysis and infrared spectroscopy. All derivatives exhibited a strong absorption in the range of 1610-1640 cm^{-1}, corresponding to the urea carbonyl. In addition, the isocyanate band at $\sim$2270 cm^{-1} was absent in the purified derivatives.

The derivatives exhibited a wide range of solubilities with the simplest derivatives (MIC and BUT) being the easiest to dissolve, while the derivatives prepared from 2,6-TDI and MDI were the most difficult. Where possible, stock solutions of the derivatives were prepared in acetonitrile. For the more refractory derivatives, stronger solvents including 1,4-dioxane and methoxyethanol were utilized. Stock solutions were diluted down for preparation of working standards in the range of 0.05 mM, based on isocyanate (or MAMA) content.

High Performance Liquid Chromatography

Chromatographic determination of the isocyanate-MAMA urea derivatives was accomplished 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 10 μL using a Pressure Lok syringe. Samples of isocyanate - MAMA ureas were chromatographed on a Supelcosil LC18 octadecyl 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 ammonium acetate buffer (0.6 % NH_4OAc, adjusted to pH 6.5 with acetic acid). The acetonitrile concentration was adjusted for determination of each isocyanate derivative with the aim of maintaining the respective retention time within a range of approximately 2.5 to 7.5 minutes. Thus for the MIC derivative, a concentration of 51% acetonitrile was utilized; for the MDI derivative, 80% acetonitrile was used. For all the other derivatives, acetonitrile concentrations between these extremes were used. For all the analyses, the mobile phase flow rate was maintained at a constant 1.0 mL per minute to ensure consistency of integrated detector response. For reference, a sample of MAMA was also analyzed chromatographically. However, in order to obtain acceptable results, more rigorous chromatographic conditions were necessary: a Supelcosil LC18-DB deactivated column of dimensions 4.6 mm i.d. x 5 cm, was used with a mobile phase of 70% acetonitrile / 3% triethylamine / 27% water, adjusted to pH 3.0 with phosphoric acid. Again the mobile phase flow was maintained at 1.0 mL per minute for comparability of results.

All chromatograms were recorded and integrated using EZ CHROM software with data collection by a Strawberry Tree I/O board installed in a Gateway personal computer.

RESULTS

Figures 1 and 2 present representative chromatograms of a MAMA sample and of a mixed sample of MAMA-derivatives of BUT, PTOL, and MDI, respectively. MAMA and each of the isocyanate derivatives were assayed by HPLC a minimum of five times. For each injection, the response factor for each of the three detection modes was calculated as the integrated peak area divided by the sample concentration in millimolarity of isocyanate group in the parent material or of MAMA. PTOL was analyzed with every group and used to account for day-to-day variability in instrumental response. Thus the integrated areas were corrected by a normalization factor based on the measured PTOL response on a given day. In general, little variability was noted from day-to-day. The PTOL derivative was also run under the chromatographic conditions used for assay of MAMA and comparable results were obtained, indicating no alteration in response by the different mobile phases used.

Table I presents the data obtained for MAMA with the three serial detection modes for a sample concentration of 0.05 mM. Response was quite intense for fluorescence and UV absorbance at 245 nm. The ratio of absorbance at 245 nm to 370 nm was equal to 12.2. This value is of particular interest as discussed below.

The normalized results for the three detection modes for the isocyanate-MAMA derivatives are shown in Tables II, III and IV, ranked in descending order. Table V presents the measured ratios of response factors for UV absorbance at 245 to that at 370 nm.

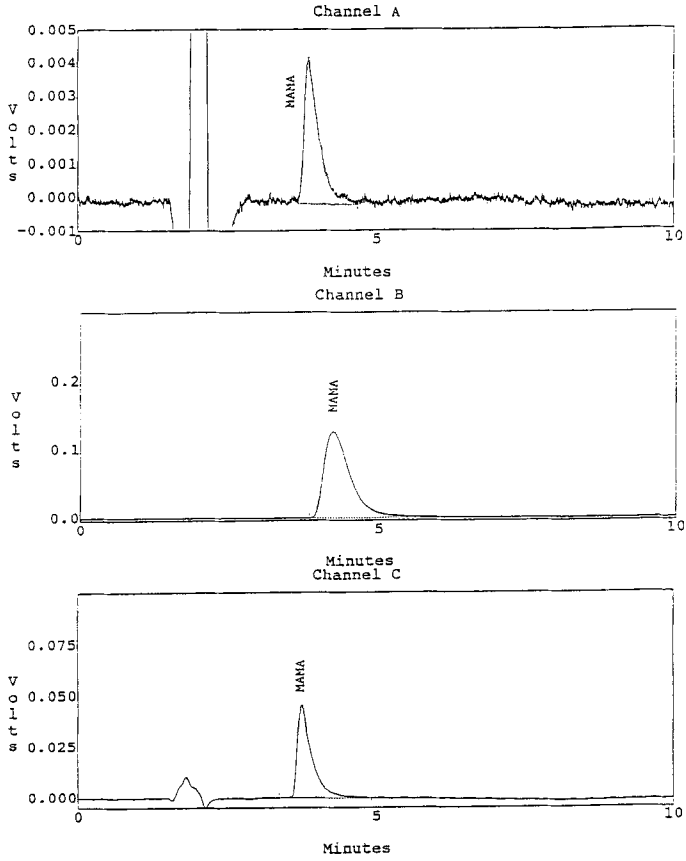


FIGURE 1 Chromatogram of 0.05 mM MAMA sample. HPLC Conditions: 5 cm x 4.6 mm i.d., Supelcosil LC18-DB column; 70% acetonitrile / 3% triethylamine / 27% water - adjusted to pH 3.0 with phosphoric acid and pumped at 1.0 mL/min. Channel A: UV absorbance at 370 nm; Channel B: fluorescence at λ_{ex} = 245 nm and λ_{em} = 414 nm; Channel C: UV absorbance at 245 nm.

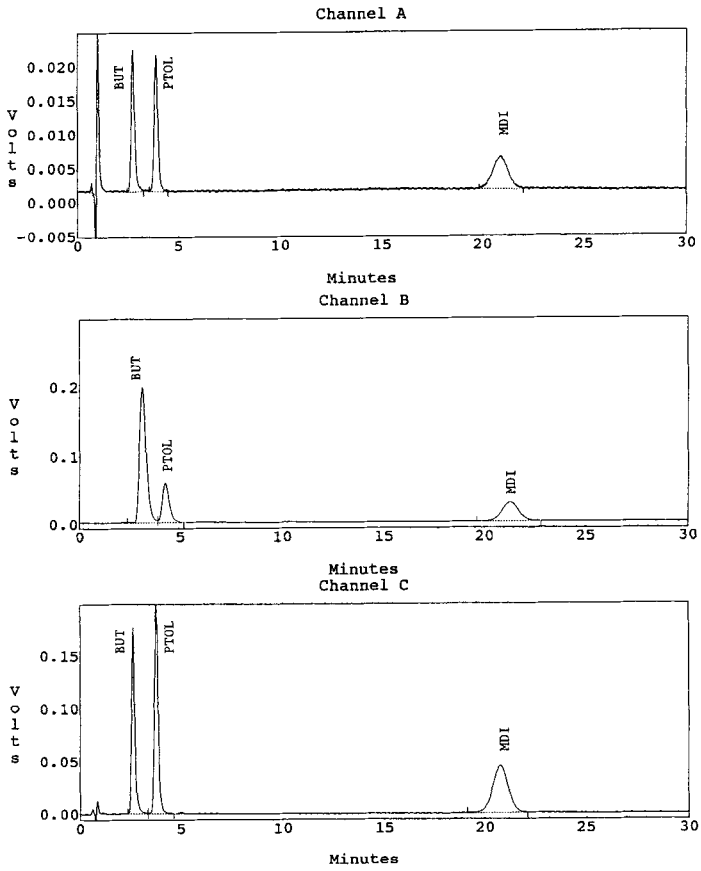


FIGURE 2 Chromatogram of mixed standard of MAMA-urea derivatives of butylisocyanate (BUT), p-tolylisocyanate (PTOL) and 4,4'-methylene-bis-(phenylisocyanate) (MDI), all 0.06 mM in TRIG. HPLC Conditions: 5 cm x 4.6 mm i.d., Supelcosil LC18 column; 62% acetonitrile / 38% buffer (0.6% aqueous NH_4OAc, adjusted to pH 6.5 with acetic acid) pumped at 1.0 mL/min. Channel A: UV absorbance at 370 nm; Channel B: fluorescence at λ_{ex} = 245 nm and λ_{em} = 414 nm; Channel C: UV absorbance at 245 nm.

TABLE I

*Measured Response Factors for Chromatographic Determination of 0.05 mM MAMA

	FLUORESCENCE 245 nm ex. 414 nm em.	UV ABSORBANCE 245 nm	UV ABSORBANCE 370 nm	RATIO UV 245/370
mean	1.53×10^8	2.59×10^7	2.13×10^6	12.2
standard deviation	1.87×10^6	6.02×10^5	2.49×10^4	0.4
n	5	5	5	5

* response factor = integrated peak area / concentration

TABLE II
Analytical Response of Isocyanate-MAMA-Urea Derivatives with Chromatographic Detection by Fluorescence

PARENT ISOCYANATE	CONCENTRATION OF NCO (mM)	n	RESPONSE FACTOR ($\times 10^{-7}$) mean ± s.d.	*HOMO-GENEOUS GROUP
MIC	0.064	6	11.05 ± 0.35	1
BENZ	0.064	5	10.95 ± 0.42	1 2
BUT	0.064	5	10.71 ± 0.39	1 2
OTOL	0.062	5	10.41 ± 0.44	2
HMDI	0.065	5	7.88 ± 0.49	3
2,6-TDI	0.063	5	7.78 ± 0.25	3
HDI	0.062	5	3.42 ± 0.11	4
MDI	0.062	6	3.35 ± 0.08	4
PIC	0.063	5	3.10 ± 0.10	4 5
PTOL	0.062	15	2.77 ± 0.13	5
2,4-TDI	0.063	5	2.77 ± 0.14	5
OVERALL	---	11	6.74 ± 3.68	---

*ANOVA: $F = 1089$, $p < 0.0001$; homogeneous groups with means not significantly different at $\alpha = 0.05$, Scheffe's Multiple Comparison Procedure.

TABLE III
Analytical Response of Isocyanate-MAMA-Urea Derivatives with Chromatographic Detection by Absorbance at 245 nm

PARENT ISOCYANATE	n	RESPONSE FACTOR ($\times 10^{-7}$) mean ± s.d.	*HOMOGENEOUS GROUP
PTOL	15	3.77 ± 0.23	1
PIC	5	3.75 ± 0.16	1 2
MDI	6	3.47 ± 0.14	1 2 3
2,6-TDI	5	3.40 ± 0.06	1 2 3 4
2,4-TDI	5	3.34 ± 0.09	2 3 4
OTOL	5	3.31 ± 0.13	2 3 4 5
MIC	6	3.18 ± 0.24	3 4 5
BUT	5	2.97 ± 0.06	4 5 6
BENZ	5	2.92 ± 0.10	5 6
HMDI	5	2.54 ± 0.16	6 7
HDI	5	2.39 ± 0.08	7
OVERALL	11	3.19 ± 0.45	---

*ANOVA: $F = 47.9$, $p < 0.0001$; homogeneous groups with means not significantly different at $\alpha = 0.05$, Scheffe's Multiple Comparison Procedure. Sample concentrations as in Table II.

All three detection modes showed statistically significant differences across isocyanates when examined by analysis of variance (ANOVA).[10] For each detection mode, there were unequal variances across the isocyanates; therefore the results of the ANOVA were verified using a Kruskall Wallis non-parametric ANOVA of the individual response factor rankings within the data set.[11] Again, the statistically significant differences among isocyanates for each detector were maintained.

Within each detector type, all possible pair-wise combinations of individual isocyanates were compared for differences using Scheffe's multiple

TABLE IV
Analytical Response of Isocyanate-MAMA-Urea Derivatives with Chromatographic Detection by Absorbance at 370 nm

PARENT ISOCYANATE	n	RESPONSE FACTOR ($\times 10^{-6}$) mean ± s.d.	*HOMOGENEOUS GROUP
2,6-TDI	5	3.32 ± 0.18	1
MIC	6	3.22 ± 0.55	1
OTOL	5	3.22 ± 0.12	1
MDI	6	3.18 ± 0.22	1
PTOL	15	3.17 ± 0.26	1
PIC	5	3.16 ± 0.13	1
2,4-TDI	5	3.09 ± 0.06	1 2
BENZ	5	2.97 ± 0.13	1 2
BUT	5	2.89 ± 0.09	1 2
HMDI	5	2.80 ± 0.15	1 2
HDI	5	2.44 ± 0.09	2
OVERALL	11	3.02 ± 0.26	---

*ANOVA: $F = 5.96$, $p < 0.0001$; homogeneous groups with means not significantly different at $\alpha = 0.05$, Scheffe's Multiple Comparison Procedure. Sample concentrations as in Table II.

comparison procedure at a significance level of 5% ($\alpha = 0.05$).[10] This resulted in the generation of the homogeneous groups (mean response not significantly different) presented in the tables. By far the widest range of response was seen with the fluorescent detector. The overall relative standard deviation of the mean response factor was 55%, with the highest value being 400% of the lowest. In addition, Scheffe's procedure indicated there were 5 separate homogeneous groups among the 11 isocyanates.

The two UV absorbance detectors were considerably more consistent across isocyanates. While both exhibited statistically significant differences

TABLE V
Ratio of Analytical Response for Isocyanate-MAMA-Urea Derivatives for Chromatographic Detection by Absorbance at 245 nm and at 370 nm

PARENT ISOCYANATE	n	RATIO OF RESPONSE FACTORS mean ± s.d.	*HOMOGENEOUS GROUP
PTOL	15	11.91 ± 0.55	1
PIC	5	11.87 ± 0.08	1 2
MDI	6	10.93 ± 0.53	1 2
2,4-TDI	5	10.83 ± 0.16	1 2
OTOL	5	10.29 ± 0.16	2 3
BUT	5	10.27 ± 0.22	2 3
2,6-TDI	5	10.27 ± 0.22	2 3
MIC	6	10.01 ± 1.02	2 3
BENZ	5	9.84 ± 0.12	2 3
HDI	5	9.80 ± 0.32	2 3
HMDI	5	9.05 ± 0.19	3
OVERALL	11	10.46 ± 0.87	---

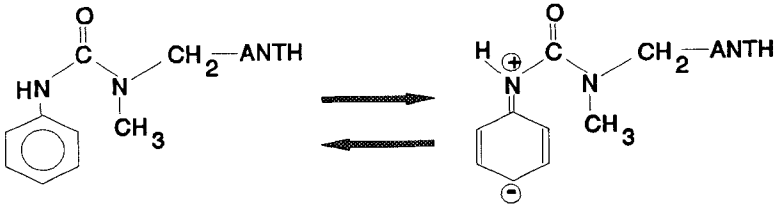
*ANOVA: $F = 24.9$, $p < 0.0001$; homogeneous groups with means not significantly different at $\alpha = 0.05$, Scheffe's Multiple Comparison Procedure.

among the isocyanates, the variability was comparatively small as measured by the relative standard deviations of the overall mean response factors - 14% for absorbance at 245 nm, and 8.6% at 370 nm.

Absorbance at 370 nm is clearly the most consistent means of measurement of isocyanate using the MAMA label. Scheffe's procedure yields only two homogeneous groups among the isocyanates. One of the two homogeneous groups contains 10 of the 11 isocyanates examined. The clear outlier is HDI; however, the range between HDI, which has the lowest

response factor, and 2,6-TDI, which has the largest, is 0.88 x 10^6, which is only 29% of the overall mean response factor.

Both the diisocyanate structure and the presence of an aromatic ring system attached to the isocyanate moiety appear to influence response by the three detection modes to varying degrees. In comparing the fluorescence response of the compounds, the data indicate that the presence of an aromatic system conjugated to the urea functionality generally results in reduction of quantum efficiency. Clearly the aliphatic monoisocyanates exhibit the least reduction of fluorescence intensity in comparison to MAMA itself (response factor of 15.3 x 10^7 for MAMA vs. a mean of 10.9 x 10^7 for the aliphatics). The derivative of BENZ however shows little additional influence on fluorescence beyond that of the aliphatics. In addition, very significant differences in response are evident for the structural isomers, PTOL and OTOL. These observations can be explained by resonance conversion of the urea group derived from the isocyanate into an iminium structure as illustrated below for the PIC derivative. The iminium resonance form provides extensive conjugation of π bonding electrons from the carbonyl through the benzene ring. The iminium structure would also be rigid and its atoms would be situated within the same plane. These properties make it likely for the iminium resonance form to reduce quantum efficiency of fluorescence of the neighboring anthracene system through internal conversion.



In comparison to the PIC derivative, the BENZ derivative has a methylene group inserted between its aromatic ring and the urea nitrogen.

This would destabilize the iminium structure and prevent extensive conjugation, thus lessening the reduction in fluorescence of the anthracene. The difference noted for the isomers of tolylisocyanate is apparently accounted for by steric effects. In OTOL, the positioning of the methyl group in the *ortho* position nearest the urea would result in steric hindrance and a reduction of the likelihood of formation of the rigid iminium structure. The geometry of PTOL places the methyl group away from the rest of the molecule so that steric hindrance is less of a factor. Indeed, the reduction in quantum efficiency of the anthracene fluorescence is similar for both PIC and PTOL. This steric effect is further reflected in the responses of the isomers of TDI in which there is extensive steric crowding in the derivative of 2,6-TDI.

The ranking of response factors for UV absorbance at 245 nm in Table III clearly indicates the enhancement of response by aromaticity with 6 of the 7 aromatic compounds showing the largest responses. Also, these same 6 aromatic compounds are grouped by Scheffe's procedure into two homogeneous groups which contain no aliphatic members. Within the aromatics and aliphatics, it also appears that the diisocyanates exhibit generally lower response. For the monoisocyanates, the aromatics and aliphatics showed mean responses of 3.44×10^7 and 3.08×10^7, respectively. Among the diisocyanates, the aromatics had a mean response of 3.40×10^7, while the two aliphatics had a mean of 2.47×10^7. These results suggest that compounds containing multiple isocyanate groups and being aliphatic in nature may exhibit significantly lower response by UV absorbance at 245 nm. This affect arises from a combination of aliphatic structures generally being non-chromogenic in the mid-UV, and of enhanced fluorescence among the aliphatics resulting in lowered *apparent* absorbance due to detection of the emitted photons.

The effect of aromaticity on absorbance at 370 nm is not straightforward. A single homogeneous group as determined by Scheffe's procedure contains 10 of the 11 isocyanates, both aromatic and aliphatic. However with the exception of MIC, there appears to be an ordering of

response by presence or absence of the aromatic structure, but the diisocyanate structure does not appear to influence the results within the aromatic compounds. The aromatic monoisocyanates show a mean response factor of 3.13×10^6. The mean response of the two aliphatic monoisocyanates is 3.06×10^6. For the diisocyanates, the difference between the aromatics and aliphatics is more pronounced. The mean response of the aromatic diisocyanates was 3.20×10^6, whereas the aliphatic diisocyanates had a mean response of 2.62×10^6. These results suggest an interaction between the diisocyanate and the aliphatic structures for absorbance at 370 nm. Again the data probably reflect enhanced fluorescence as well as reduced absorbance since a fluorescence excitation maxima also occurs at 370 nm.

The ratios of response factors for UV absorbance at 245 nm and 370 nm is of special interest and could be useful for *identification* of TRIG compounds. These data are presented in Table V. ANOVA indicates statistically significant differences in this ratio among the isocyanates; Scheffe's procedure yields 3 homogeneous groups, with one of the groups containing 9 of the 11 isocyanates. However, the relative standard deviation of the overall mean ratio is only 8.3% There appears to be an ordering of the ratios according to the presence or absence of aromaticity in the parent isocyanate, although Scheffe's procedure places only 4 of the 7 aromatic compounds into a homogeneous group containing no aliphatic members. Nonetheless, this is consistent with the observation that UV absorbance at 245 nm appears to be influenced more than that at 370 nm by the presence of aromaticity. Thus the aromatic compounds had a mean ratio of 10.85 whereas the aliphatics had a mean of 9.78.

DISCUSSION & CONCLUSIONS

The purpose of this work was to evaluate the potential for using MAMA as a chemical label for TRIG. 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 methoxy-phenylpiperazine (MOPIP) in solution in an impinger for collection of airborne TRIG. All TRIG compounds react with the MOPIP to form urea derivatives which absorb in the UV, and 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 on the HPLC chromatogram can be identified as a specific TRIG oligomer using the specific monomer as a standard. Total TRIG content of a sample can be estimated from combining the electrochemical response of all peaks, and comparing it 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.[12,13] 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 TDI and ethylene glycol result in an inconsistent ratio of response by electrochemical to UV absorbance detection as the number of polymer units increases.[14]

Little work has been done on the determination of TRIG using 9-(N-methylaminomethyl)-anthracene (MAMA) as the derivatizing agent. The method was applied with some success to measure isocyanate monomer and oligomer in paint overspray,[15] and TRIG from thermal degradation of polyurethane binders.[16]

In this work a systematic approach has been taken in order to evaluate potential structure / response trends in assessing TRIG using MAMA with analysis by HPLC. The results have indicated that the ratio of response by

UV absorbance at 245 and 370 nm is relatively constant regardless of the structure of the isocyanate parent material. This coupled with the fact that the TRIG-MAMA derivatives are intensely fluorescent, provides a potentially powerful approach to discriminating unknown TRIG forms from other materials in real samples. The ability to identify TRIG forms based on these detection modes can be further refined if there is knowledge of whether aromatic or aliphatic compounds are present.

In addition to identification of TRIG, reasonably accurate quantitation can be achieved using detection at 370 nm. For these purposes, the use of MAMA itself as a standard material cannot be recommended. The material is difficult to chromatograph as the free amine and it also is somewhat labile, undergoing photodecomposition.[7] One of the isocyanate monomer derivatives, which are easily synthesized in the laboratory and are fairly stable when protected from light,[7] could reliably be used as a standard material for unknown TRIG. For this work, the PTOL derivative was used as a reference compound with success. However for quantitation of TRIG using absorbance at 370 nm, the BENZ derivative of MAMA would appear to be the best choice since its response factor falls roughly in the middle of the range seen among the test compounds.

In summary, the use of MAMA as a derivatizing agent, coupled with analysis by HPLC with UV absorbance and fluorescence detection, is a promising approach to the identification and quantitation of airborne TRIG. The UV absorbing properties of a series of MAMA derivatives prepared from representative isocyanate compounds was remarkably consistent and primarily dependent upon the number of MAMA units in the resulting compound. The fluorescence response was found to be quite variable and correlated in large part with structural properties. Nonetheless it is a useful adjunct to UV absorbance detection for confirmation of suspect TRIG compounds. Further evaluation of the method for various oligomeric and polymeric materials containing free isocyanates is warranted. These studies are currently being conducted and will be presented in further installments in this series of papers.

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