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Evaluation of 1-(9-anthracenylmethyl) piperazine for the Analysis of Isocyanates in Spray-Painting Operations

AUTHORS
Walter E. Rudzinski[a]
Sam Norman[a]
Bruce Dahlquist[b]
Kurt W. Greebon[c]
Andy Richardson[c]
K. Locke[c]
Tom Thomas[c]

[a]Department of Chemistry, Southwest Texas State University, San Marcos, TX 78666;
[b]HQ AFIA/SGM, 9700 G Avenue SE, Suite 316B, Kirtland AFB, NM 87117-5670;
[c]AL/OEA, Brooks Air Force Base, San Antonio, TX 78235-5501

A new reagent, 1-(9-anthracenylmethyl)piperazine (MAP), was used for the derivatization of airborne 1,6-hexamethylene diisocyanate (HDI) and polyisocyanates generated during spray-painting operations. The new reagent, which offers enhanced sensitivity and uniformity of response to both the monomeric and oligomeric forms of HDI, was compared directly with 1-(2-methoxyphenyl)piperazine (MOP), the currently employed derivatizing reagent used in the National Institute for Occupational Safety and Health Method 5521. Both the validity of the side-by-side sampling protocol and the efficacy of two derivatizing reagents were evaluated in field studies. The analytical results indicate that there is no significant difference at the 95% confidence level in the concentration of polyisocyanate in the aerosol as determined by two impingers containing MAP and a third containing MOP when these are positioned in a side-by-side-by-side arrangement.

Keywords: 1,6-hexamethylene diisocyanate (HDI), 1-(9-anthracenylmethyl)piperazine (MAP), spray-painting

Isocyanates generated during polyurethane spray-painting operations are hazardous, and a number of sampling and analysis approaches have been developed to ascertain the amount of diisocyanate monomer present. The area has been reviewed several times.(1–3) Recently, considerable effort has been expended in the development of samplers that will quantitate total isocyanate present both in the monomer and oligomer forms.(4) Promising derivatizing reagents include 1-(2-methoxyphenyl) piperazine (MOP),(5) 9-(methylaminomethyl)anthracene (MAMA),(6) and tryptamine (TRY).(7)

Recently, a new derivatizing reagent, 1-(9-anthracenylmethyl) piperazine (MAP)(8) has been prepared that improves on the analytical figures of merit associated with the previous reagents. MAP reacts as rapidly as MOP with phenyl isocyanate and more rapidly than TRY and MAMA.(9) This is advantageous, since this reactivity in the sampling device will prevent losses of isocyanate group to competing reactions with water and polyols. The ultraviolet (UV) intensity of MAP is similar to that of MAMA and much better than that of TRY and MOP, while the average intensity of fluorescence response for MAP is about the same as that of MAMA but substantially greater than that of TRY ureas. This means that isocyanates derivatized with this reagent will be detectable at very low levels.(9) The fluorescence variability among the ureas of diisocyanates (about 20% relative standard deviation), though low for all the ureas of MAP, MAMA, and TRY, still is not low enough to quantitate an unknown isocyanate derivatized with any of these reagents. However, the fluorescence response can still be used for qualitative identification under these circumstances. With the previous characteristics attributable to MAP, the authors decided to test it in actual spray-painting operations.

MAP was evaluated in a series of side-by-side studies designed to evaluate both the side-by-side sampling protocol and the new derivatizing reagent. Two impingers filled with solutions of MAP were compared with each other and with a third impinger filled with a solution of MOP (the current sampling approach, which served as a benchmark).

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EXPERIMENTAL

Reagents and Apparatus

MOP was obtained from Fluka, and MAP was synthesized and purified according to the procedure described by Streicher.(9)

The 98% pure 1,6-hexamethylene diisocyanate (HDI) monomer was purchased from Kodak. Desmodur N-75, which is 75% HDI-based polyisocyanate in xylene and contains 35–40% biuret trimer of HDI (material safety data sheet), was obtained from Bayer (Pittsburgh, Pa.). Bulk polyurethane paint hardener was obtained from Deft (Irvine, Calif.) and contains 60% aliphatic polyisocyanate and 40% organic solvents (material safety data sheet). All other chemicals and solvents were reagent grade or better.

Standard midget impingers filled to 15.0 mL with a solution of MOP in toluene (43 mg/L) or filled to 25.0 mL with a solution of MAP in dimethylsulfoxide (62 mg/L) were used to collect isocyanate. Dupont Alpha 1 pumps were used to draw the air samples. The pumps were calibrated both before and after analysis with a Gillian bubble generator.

The high performance liquid chromatograph (HPLC) system consisted of a Hewlett-Packard Series 1090 chromatograph with autosampler and diode array UV-VIS detector operated at 245 nm for MOP and 257 nm for MAP. A Hewlett-Packard 1049A electrochemical detector operated in the amperometric mode at +0.8 V was connected in series with the HPLC. Hewlett-Packard 3396 Series II integrators were used to determine the area under the chromatographic peaks.

A Hewlett-Packard Lichrosorb RP 18 10 μ (200 × 4.6 mm) column and (45/55) acetonitrile/methanolic buffer (pH=6.0) mobile phase were used for analyzing the MOP derivatives. A Hewlett-Packard Lichrosorb RP 8 10 μ (200 × 4.6 mm) column and (58/42) acetonitrile/0.04 M sodium phosphate buffer adjusted to a pH of 2.85 with phosphoric acid were used for analyzing the MAP derivatives. To speed up the analysis of MAP derivatives, the pH was also adjusted to 2.5. The injection volume of sample was consistently 20 μL.

Preparation of Standards

HDI-MOP:N,N'-bis [4-(2-methoxypheny)piperazine-1-carbonyl] -1,6-hexamethylenediamine standards were prepared as described in National Institute for Occupational Safety and Health (NIOSH) Method 5521.(5) HDI-MAP:N,N'-bis [4-(9-anthracenylmethyl) piperazine-1-carbonyl]-1,6-hexamethylenediamine standards were prepared as in the procedure described by Streicher.(9)

The Deft hardener, after "blow-down" of the solvent, was used to prepare HDI-based polyisocyanate-MOP urea and HDI-based polyisocyanate-MAP urea standards. The polyisocyanate urea stock solutions (1000 μg/mL) were prepared by mixing 0.025 g of the hardener in 25 mL of toluene with 0.050 g of either MOP or MAP derivatizing reagent in toluene. 70 μL of acetic anhydride was then added to acetylate the excess derivatizing reagent. The solution was evaporated to dryness and reconstituted to 5.0 mL with methanol for the MOP-based urea or with 25.0 mL of dimethyl sulfoxide (DMSO) for the MAP-based urea.

HDI-based polyisocyanate-MOP urea standards were also prepared based on Desmodur N-75 and the Deft hardener that had not been "blown down." HPLC analysis of the Desmodur N-75, Deft hardener, and Deft hardener "blown down" indicated that the constituent polyisocyanate in the samples was the same (identical retention time for the major peak), and that the peak areas corresponding to the Deft hardener and Desmodur N-75 were 56.3% and 72.5%, respectively, of the area of the Deft hardener that had been "blown down." These percentages correspond very closely to the reported values of polyisocyanate on the material safety data sheets (60% for the Deft hardener and 75% for Desmodur N-75). This internal self-consistency led the authors to believe that the major peak observed in the chromatogram of the Deft hardener (80% of the total area not attributable to solvent or acetylated MOP) would be a suitable standard for analyzing HDI-based polyisocyanates in the field.

Working standards were prepared by serial dilution from the stock and ranged from 2–1000 μg/mL.

Description of Spray-Paint Operations

Three different spray-paint operations (six sampling events) were evaluated at Keesler Air Force Base, Miss. Operation 1K involved painting a blue van in a drive-in spray-paint booth. Operations 2K and 3K involved spray-painting a C-130 aircraft engine and power generator, gray and green, respectively, in a three-sided spray-painting area with a waterfall air cleansing system at the front of the bay.

A high-pressure spray gun was used for operation 1K. High-volume low-pressure (HVLP) spray guns were used in operations 2K and 3K. All spray-painting operations were batch, performed by different painters who used supplied-air hoods to cover the head and Tyvek® suits to cover the body.

In all spray-painting operations Deft polyurethane paint formulations were used with pigment:hardener in a 1:1 ratio.

Sampling Strategy

Area sampling was performed by positioning two impingers containing MAP in DMSO next to each other and adjacent to a third impinger containg MOP in toluene. The three inlets were positioned in line, with each about 10–11 cm (4–4.5 inches) away from the next. The air sampling interval for the two impingers containing MAP was always the same.

Samples were collected in an area in which the painter routinely does not work, but in an area of overspray. For all operations, area samplers were positioned 1.2–1.4 m (4–4.5 ft) above the floor and about 1.5–1.8 m (5–6 ft) downdraft from the equipment being painted. For operations 2K and 3K area samplers were positioned in front of the waterfall.

The sampling protocols described in NIOSH Method 5521 were used throughout. The isocyanate samples were collected at an airflow rate of 1.0 L/min. Sampling times ranged from 10–63 min.

After collection the isocyanate samples in MOP-toluene were immediately refrigerated at 4°C; the samples in MAP-DMSO were maintained at room temperature. Both were then shipped in screw-cap vials within two days of sampling. On arrival at the analytical lab the samples were refrigerated, then prepared for analysis within three days.

Analysis

To compare the results obtained for HDI monomer and HDI-based polyisocyanate using the two methods, both were quantitated using the UV detector response. The electrochemical detector (EC) was used for confirmation of identity only, except in a few cases where there was an interference with the polyisocyanate peak in the UV chromatogram. In such cases the EC detector response was used for quantitation. The EC/UV detector response for a series of HDI-based polyisocyanate standards was about 40 for the MOP derivatives and 28 for the MAP derivatives.

The concentration of isocyanate in field samples was determined by using the area under the largest peak in the chromatogram of a sample and comparing it with the area under the largest peak in the chromatogram of a standard based on HDI monomer or bulk hardener.

All HDI-based polyisocyanate-MOP urea samples were run within four days of receipt. HDI-based polyisocyanate-MAP ureas were run for the first time within 48 hours of the analysis of the HDI-based polyisocyanate-MOP ureas.

Results and Discussion

HDI monomer concentrations during spray-paint operations were all below the limit of detection whether using MOP or MAP as the derivatizing reagent. Although MAP has a molar absorptivity five times as high as that of MOP,(9) the sensitivity advantage associated with MAP was obviated because of the large tailing associated with the acetylated-MAP derivatizing reagent. Repeated efforts to extract the HDI-MAP urea peak from the acetylated-MAP tail were ineffective.

HDI-based polyisocyanate concentrations were easily accessible with either the MAP or MOP reagents. The chromatograms in Figure 1 show the excellent resolution obtained for the separation of the polyisocyanate MOP and polyisocyanate MAP ureas from the acetylated derivatizing reagent and other interferents in a real sample.

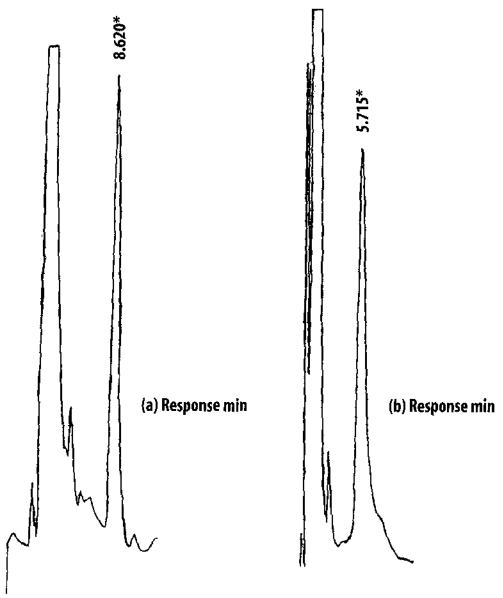

FIGURE 1. High performance liquid chromatograms. Separation of (a) HDI-based polyisocyanate-MOP urea (Sample 278MOP[14L]) and (b) HDI-based polyisocyanate-MAP urea (Sample 276MAP[63L]). The derivatized isocyanate is marked with an asterisk. Both samples were obtained during the same spray-painting event. All sampling and chromatographic conditions are as reported in the Experimental section of text.

Calibration curves based on HDI-MOP urea and HDI-MAP urea were linear, with an $R^2 > 0.99$ based on a working range of 0.5 to 5.0 μg/mL. The analytical sensitivity was $1.4 \times 10^5/(\mu g/mL)$ for the HDI-MOP urea, and about five times as large for the HDI-MAP urea. The HDI-MOP and HDI-MAP ureas had estimated detection limits of 0.1 and 0.03 μg/mL, respectively.

All calibration curves based on polyisocyanate ureas were linear within the working range of 1–20 μg/mL with an $R^2 > 0.997$ and an estimated detection limit (defined as three times the standard deviation) of 0.5 μg/mL for each. The analytical sensitivity was $4.4 \times 10^4/(\mu g/mL)$ for HDI-based polyisocyanate-MOP urea, and $2.7 \times 10^5/(\mu g/mL)$ for HDI-based polyisocyanate-MAP urea. The latter urea has a sensitivity about six times as great as the former because of the increased molar absorptivity associated with the pendant anthracenyl moiety.

Table I reports the polyisocyanate air concentrations in mg/m^3 obtained during six sampling events conducted during three different spray-paint operations (two sampling events per spray-paint operation). Further, three samplers were positioned side-by-side-by-side during each sampling event. The data for a total of 17 of 18 samples are reported in Table I. One sample spilled and was not included in the data. Columns 3–6 represent the results obtained when analyzing the same polyisocyanate MAP urea over a period of 10 days. Each sample was run at least twice on different days. Run 3 and Run 4 were extra runs that were needed to confirm the results for Samples 527MAP, 531MAP, and 529MAP. For Samples 527MAP and 531MAP, the first and second runs did not yield reproducible results; whereas, for 529MAP, the authors wanted to assess whether 7 or 4.6 mg/L was the true value. For these reasons, polyisocyanate MAP urea samples from operation 3K were run a third and fourth time. Samples 273MAP, 274MAP, 276MAP, and 277MAP were run more than twice to give additional data pairs to evaluate the side-by-side sampling. Column 7 represents the average value for the polyisocyanate-MAP urea sample based on all the analytical runs. Column 8 gives the value obtained for the polyisocyanate-MOP urea using the benchmark NIOSH method 5521.

Results from repetitive runs indicate that for samples taken during operation 1K, there is on average a 10% decrease in the analytical concentration of the polyisocyanate-MAP urea over a period of 10 days. For operations 2K and 3K the analytical concentration declines precipitously by about 40% in three days even if the sample is stored at 4°C. The stability of HDI-based polyisocyanate-MOP ureas was previously assessed and it was found that for a reanalysis of 12 polyisocyanate-MOP urea samples, after two weeks, the new value was within 25% of the original.(10)

All results obtained from a given analytical determination performed on a particular day, for two side-by-side MAP impingers, are represented within a box. The average absolute deviation from each other for the 12 data pairs is 0.38 mg/m^3 (n=12), which is less than 0.65 mg/m^3 (n=14), the average absolute deviation from the mean for a sample when run on different days over a period of 10 days. The relative pooled standard deviation from the mean for the side-by-side MAP impingers for each sampling event varies from a low of 3% for 1K (6-21-9), to a high of 16% for 2K (6-27-14) with 9% as the average relative standard deviation. The relative standard deviation for two side-by-side samplers is much smaller than the relative standard deviation from the mean for a sample when run on different days over a 10-day period. This result varies from a low of 3% for 1K (6-21-11) to a high of 35% for 2K (6-27-14) with an average of 20%. The results suggest that for these spray-painting operations, the average spatial variation in the concentration of polyisocyanate is smaller than the variations that are observed when running the same sample over an extended period of time. The small average relative standard deviation seems to validate the protocol that uses two impingers side-by-side for comparing sampling devices.

The average polyisocyanate concentration in air as measured by the polyisocyanate-MAP urea response varied between 1.1 and 6.1 mg/m^3 (see column under MAP). The polyisocyanate concentration as measured by the polyisocyanate-MOP urea response varied between 1.4 and 4.6 mg/m^3 (see column under MOP). All of the values exceed 1 mg/m^3, which is the short-term exposure limit recommended by the manufacturer (Bayer) and the ceiling stan-

TABLE I. Polyisocyanates in the Spray-Paint Environment

Sampling Event Op[B] (mo-day-time)	Sample #Reagent[C] (volume)	mg/m³ of HDI-Based Polyisocyanate[A] Run 1[D] 7-17	Run 2[D] 7-20	Run 3[D] 7-24	Run 4[D] 7-27	MAP[D]	MOP[E]
1K (6-21-9)	273MAP (62L)	6.5	6.7	6.1	5	6	
	274MAP (60L)	6.3	6.8	6	5.4	6.1	
	275MOP (11L)						4.6
1K (6-21-11)	276MAP (63L)	5	5.1		4.8	5	
	277MAP (61L)	4.6	4.7		4.9	4.7	
	278MOP (14L)						4.4
2K (6-27-14)	156MAP (21L)	3.7	2.2			3	
	157MAP (20L)	4.6	2.8			3.7	
	158MOP (23L)						3.6
2K (6-27-15)	159 MAP (42L)	1.9	1.2			1.5	
	160MAP (42L)	2	1.4			1.7	
	161MOP (47L)						1.4
3K (7-11-9)	527MAP (39L)	—	1.2	1	—	1.1	
	528MOP (39L)						1.7
3K (7-11-10)	531MAP (11L)	5.9	—	—	6.2	5.9	
	529MAP (10L)	7	4.6	4.3	—	5.4	
	530MOP (11L)						3.1

[A]Boxed entries indicate results obtained from a given analytical determination performed on a particular day, for two side-by-side MAP impingers.

[B]op = operation; (mo-day-time) = month-day-time of sampling

[C]Reagent (volume) = Armstrong Lab sample number followed by the acronym for the derivatizing reagent followed by the volume of sampled air

[D]Run number with month and day below = individual analytical determinations

[E]MAP and MOP = average concentrations obtained with the reagent

dard established by the State of Oregon's Occupational Safety and Health Administration.(11) At present, there are no federal Occupational Safety and Health Administration permissible exposure limits or short-term exposure limits, no NIOSH recommended exposure limits, and no American Conference of Governmental Industrial Hygienists' threshold limit values(12) for polyisocyanates, although polyisocyanates in an aerosol form may be inhaled during spray-painting operations,(13,14) and some early reports suggest that polyisocyanates can cause occupational asthma during spray painting.(15–19)

For each sampling event, the average of the results obtained from two MAP impingers was paired with the result obtained from an adjacent MOP impinger (10–11 cm away). The Wilcoxon Signed Rank test, which can be used as a nonparametric alternative to the paired t-test, was then used to evaluate the results based on the data set containing six paired values. The results indicate no significant difference ($p<0.05$).(20) The coefficient of correlation for the data is 0.879, which implies a positive correlation between the two methods.

For five of six sampling events the results for two MAP impingers next to each other were compared. For sampling event 3K (7-11-9) a comparison of two side-by-side MAP impingers was not available because one of the impingers spilled. The paired t-test was used to evaluate the five remaining data pairs. This test is appropriate because the data should have a normal distribution. The results indicate no significant difference ($p<0.05$).(20)

REFERENCES

1. **Melcher, R.G.:** Industrial hygiene. *Anal. Chem. 55*:40R–56R (1983).
2. **Purnell, C.J. and R.F. Walker:** Methods for the determination of atmospheric organic isocyanates. A review. *Analyst 110*:893–905 (1985).
3. **Research and Development Laboratories:** *Analysis of Isocyanates in Spray Paint Operations,* (RDL 34) by W.E. Rudzinski. Culver City, CA: Research and Development Laboratories, 1992.
4. **Streicher, R.P., E.R. Kennedy, and C.D. Lorberau:** Strategies for the simultaneous collection of vapours and aerosols with emphasis on isocyanate sampling. *Analyst 119*:89–97 (1994).
5. **National Institute for Occupational Safety and Health (NIOSH):** Isocyanates (Method 5521), by M.J. Seymour and A.W. Teass. In *Manual of Analytical Methods,* 3rd ed., vol. 2 (pub. no. 84-100). Washington, DC: U.S. Department of Health and Human Services, 1989.
6. **Sango, C. and E. Zimerson:** A new reagent for determination of isocyanates in working atmospheres by HPLC using UV or fluorescence detection. *J. Liq. Chromatogr. 3*:971–990 (1980).
7. **National Institute for Occupational Safety and Health (NIOSH):** Isocyanates (Method: 5522), by R.J. Key-Schwartz and S.P Tucker. In *Manual of Analytical Methods,* 4th ed. Washington, DC: U.S. Department of Health and Human Services, 1993.
8. **Streicher, R.P.:** Method of Detecting Isocyanates, U.S. Patent No. 5,354,689. Oct. 11, 1994.
9. **Streicher, R.P., J.E. Arnold, M.K. Ernst, and C.V. Cooper:** Development of a novel derivatization reagent for the sampling and analysis of total isocyanate group in air and comparison of its performance with that of several established reagents. *Am. Ind. Hyg. Assoc. J. 57*:905–913 (1996).
10. **Rudzinski, W.E., B. Dahlquist, S. Svejda, A. Richardson, et al:** Sampling and analysis of isocyanates in spray-painting operations. *Am. Ind. Hyg. Assoc. J. 56*:284–289 (1995).
11. **Janko, M., K. McCarthy, M. Fajer, and J. van Raalte:** Occupational exposure to 1,6-hexamethylene diisocyanate-based polyisocyanates in the state of Oregon, 1980–1990. *Am. Ind. Hyg. Assoc. J. 53*:331–338 (1992).
12. **American Conference of Governmental Industrial Hygienists (ACGIH):** *Threshhold Limit Values and Biological Exposure Indices for 1986-1987.* Cincinnati, OH: ACGIH, 1987.
13. **Hardy, H. and J. Devine:** Use of organic isocyanates in industry. Some industrial hygiene aspects. *Ann. Occup. Hyg. 22*:421–427 (1979).
14. **Silk, S.J. and H.L. Hardy:** Control limits for isocyanates. *Ann. Occup. Hyg. 27*:333–339 (1983).
15. **Belin, L., U. Hjortsberg, and U. Wass:** Life-threatening pulmonary reaction to car paint containing a prepolymerized isocyanate. *Scand. J. Work, Environ. Health 7*:310–312 (1981).
16. **Malo, J.L., G. Ouimet, A. Cartier, D. Levitz, et al.:** Combined alveolitis and asthma due to hexamethylene diisocyanate (HDI), with demonstration of crossed respiratory and immunologic reactivities to diphenylmethane diisocyanate (MDI). *J. Allergy Clin. Immunol. 72*:413–419 (1983).
17. **Nielsen, J., C. Sango, G. Winroth, T. Hallberg, et al:** Systemic reactions associated with polyisocyanate exposure. *Scand. J. Work, Environ. Health. 11*:51–54 (1985).
18. **Vandenplas, O., A. Cartier, J. LeSage, Y. Cloutier, et al:** Prepolymers of hexamethylene diisocyanate as a cause of occupational asthma. *J. Allergy Clin. Immunol. 91(4)*:850–861 (1993).
19. **Tornling, G., R. Alexandersson, G. Hedenstierna, and N. Plato:** Decreased lung function and exposure to diisocyanate (HDI) and (HDI-BT) in car repair painters; observations on re-examination 6 years after initial study. *Am. J. Ind. Med. 17*:299–300 (1990).
20. **Cotton, T.:** *Statistics in Medicine.* Boston, MA.: Little, Brown and Co., 1974.