IV. ENVIRONMENTAL DATA

Environmental Concentrations

Area monitoring of the startup and on-line procedures for TDI synthesis during the 1st year of production in a new manufacturing plant was conducted by Weill et al [92]. TDI concentrations were determined using commercially available continuous-tape area monitors that had been calibrated against results obtained by the Marcali method [111]. During the startup procedures, the mean weekly TDI concentrations for the synthesis, finishing, and drummming areas were 5.6, 17.3, and 11 ppb (39, 122, and 78 μg/cu m), respectively. The respective maximum excursion concentrations were 7.1, 20.5, and 12.9 ppb (50, 146, and 92 μg/cu m). The initial on-line production concentrations for the three areas were 11.3, 16.4, and 7.5 ppb (80, 116, and 53 μg/cu m) with respective excursions to 13.8, 21.1, and 8.8 ppb (98, 150, and 62 μg/cu m). When 8-hour TWA concentrations for the entire plant were analyzed for the 11 months of monitoring, it was found that the 1973 NIOSH-recommended TWA concentration limit of 5 ppb (35 μg/cu m) was exceeded on approximately half of the days.

More recent studies of the same plant by Dharmarajan et al [112] compared the results of the area monitoring with values obtained by continuous-tape personal monitoring. Both monitoring methods were used simultaneously during some period each day for 22 months. When 8-hour TWA values were analyzed, no positive correlation could be found between personal and area sampling. Area monitoring, then, did not seem to accurately reflect actual individual exposures.

Hervin and Thoburn [100] reported that concentrations of airborne TDI were below the TLV of 20 ppb (140 μg/cu m) in an aircraft overhauling facility where the painters sprayed aircraft with polyurethane paints. Area and personal samples were analyzed by the thin-layer chromatographic method of Keller et al [113]. The concentrations of airborne TDI near the aircraft fin, near the wing, on the floor where mixing was done, and on the floor midway between the two bays were <30, <20-30, 20, and <20 μg/cu m (<4, <3-4, 3, and <3 ppb), respectively. The corresponding concentrations of HDI were 40-100, <30-60, <20-300, and <20 μg/cu m (6-15, <4-9, <3-45, and <3 ppb). Thirteen personal samples taken at various operations contained TDI at concentrations of 40 μg/cu m or less. Corresponding HDI concentrations ranged from less than 30 to 300 μg/cu m.

In an operation where polyurethane foam lines were used to make automobile seat cusions, Butler and Taylor [114] detected no TDI in the areas where TDI pouring, heat curing, molded product removal, mold cleaning, and molded product trimming took place. Vandervort and Shama [93] of NIOSH recorded TDI at 5-31 μg/cu m (0.7-4.3 ppb) during foaming operations in a plant manufacturing picnic jugs, ice chests, and metal vacuum bottles. Air collected from the breathing zones

of several foaming operators contained up to 40 µg/cu m of TDI, ie, the concentrations were lower than the present Federal standard of 20 ppb (140 µg/cu m).

HDI concentrations measured by Filatova et al [76] were 0-100 µg/cu m (0-15 ppb) in all the departments of a plant manufacturng HDI. However, concentrations of 200-240 µg/cu m (30-35 ppb), which exceeded the USSR MAC of 50 µg/cu m (7 ppb), were recorded while spills were being cleaned up.

Konzen et al [60] measured concentrations of MDI while preexpanded polyurethane foam was applied for 2.3-10 minutes at four locations in an underground mine. Unfiltered air samples were collected 5, 25, 50, and 75 feet away from the spray operation, and prefiltered air samples were also collected 5 feet away. Air samples were collected for 2.2-30 minutes at a flowrate of 1.0 liter/minute. The air samples were analyzed by the Marcali method [111]. The data showed that the concentration of airborne MDI decreased with increasing distance from the spray. When the mine shaft air ventilation rate was 8 feet/minute, an MDI concentration of 1,360 µg/cu m (133 ppb) was found at 5 feet and 160 µg/cu m (16 ppm) was found at 75 feet from the source of the spray [60]. At an air ventilation rate of 100 feet/minute, the concentration of airborne MDI downstream was reduced from 2,290 µg/cu m (224 ppb) 8 feet from the spray to 1,320 µg/cu m (130 ppb) 50 feet away.

Collecting air through membrane filters with an average pore diameter of 0.8 µm removed approximately 80% of the reactive MDI found 5 feet from the spray [60]. Light and electron microscopic examination of polyurethane foam particles trapped on the membrane filters showed that over 98% of them were less than 3 µm in diameter and that about 85% were less than 1 µm.

Fitzpatrick et al [115] conducted a survey of workers applying polyurethane foam containing MDI to the walls of an underground mine. Unfiltered air samples were collected 5, 10, 25, 50, and 100 feet downstream from the spray operation, and a few prefiltered samples were also collected. Air samples were collected for up to 30 minutes with the ventilation velocity in the mine at 60 feet/minute, and the samples were analyzed by the Marcali method. The results showed that concentrations of airborne MDI decreased with increasing distance from the spray operation. A portable aerosol photometer and a cascade impactor were used to determine the concentration and size of particles produced during the generation of the polyurethane foam. About 73% of the particles were 1-2 µm in diameter.

Fitzpatrick et al [115] stated that most of the MDI detected in the air was carried by this particulate matter in the reactive form. The reaction of MDI with other components of the foam was complete within about a minute, or 60 feet downstream from the spraying operation.

Dharmarajan and Weill [116] found that approximately 90% of the MDI present in air during a foam spray operation was blocked by passage through glass fiber or

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Teflon filters (0.5 µm pore diameter). The percentage blocked was independent of MDI concentration in the range 20-550 µg/cu m, a finding that supports the contention that most airborne MDI is present in particulate form. Furthermore, they found that approximately 50% of the particles were less than 10 µm in diameter. Assuming that all MDI in the air is in the form of aerosols and assuming an equal collection efficiency for simultaneous sampling of particulates on a filter and MDI in an absorber, the authors found that MDI constituted 3.03-20.34% of the mass of the airborne dust collected on a filter.

Vandervort and Lucas [61] measured concentrations of airborne MDI during foaming operations in a factory that manufactured fibrous glass tanks. One of four breathing-zone samples analyzed for MDI by a Marcali method [94] showed that a foam operator was exposed to MDI at 12 ppb (120 µg/cu m) for 30 minutes. Concentrations of airborne MDI in 16 of the 38 samples taken during foam application ranged from undetectable to 26 ppb (260 µg/cu m). The concentrations of airborne MDI were highest within 3 feet of the point of application. Two samples taken less than 3 feet from the operation 20 minutes after foaming stopped showed airborne MDI at 3 ppb (30 µg/cu m). Analysis of 71 air samples collected over an average of 6.5 hours from the breathing zones of 18 employees showed that workers were exposed to other contaminants, such as methylene chloride, toluene, and acetone, at concentrations of a few ppm and to airborne styrene at 18-130 ppm.

In the end-cap area, 13 samples taken during and directly after foaming showed MDI concentrations averaging 4 ppb [61]. One sample taken from the chemical assembly area during foaming showed that the foam operator was exposed for 8 minutes to MDI at 25 ppb (250 µg/cu m), and three samples collected within 3 feet of foaming showed MDI concentrations ranging from 0 to over 1,000 ppb, presumably the limit of the analytical procedures used. Two samples collected during the first 30 minutes after foaming showed only residual amounts of MDI. Eighteen more breathing-zone samples from 12 employees in the foaming, chemical assembly, and end-cap areas and the corresponding 18 area samples showed that MDI exposures ranged from 0 to 11 ppb (110 µg/cu m). The highest concentrations were found in samples from foam operators, and other employees were exposed to MDI at less than 5 ppb (50 µg/cu m). Area samples indicated that MDI concentrations ranged from 3 to 25 ppb (30-250 µg/cu m) within 3 feet of foaming operations and from 0 to 15 ppb beyond this area.

In another NIOSH health hazard evaluation, Bodner et al [96] measured the concentrations of airborne MDI in a fibrous glassing area where a foaming operator sprayed tubs and showers with a foaming agent. According to the supplier, the foaming agent contained no TDI. Analysis of area samples showed that the areas adjacent to the foam gunner and to the last roller in the assembly line had concentrations of airborne MDI of 150 and 10 µg/cu m (15 and 1 ppb), respectively. Analyses of breathing-zone air showed that the foam gunner in the area was exposed to MDI at an average of 230 µg/cu m (23 ppb), a concentration exceeding the present Federal standard of 20 ppb (200 µg/cu m).

Tubich [14] measured air concentrations of MDI generated in foundry operations, where it is present as a component of an oil-base no-bake binding system. The author did not describe the collection of samples or identify the analytical method used. No measureable MDI concentrations were found in 10 samples from the mixing operation and 12 from the molding operation; both operations are conducted at room temperature. Ten samples from the torching or oven-drying operation also showed no MDI, and 17 mold-pouring samples showed less than 7 ppb (70 µg/cu m); these operations involve elevated temperatures, and the author attributed the low concentrations to the brevity of the operations, which did not permit significant vapor concentrations to be generated. Mean concentrations of MDI exceeded the Federal limit of 20 ppb (200 µg/cu m) in shakeout and core knockout operations; MDI was present in 25 shakeout samples at 2-160 ppb (20-1,600 (µg/cu m), and in 9 core knockout samples at 6-66 ppb (60-660 µg/cu m).

Engineering Controls

The engineering controls recommended for all diisocyanates in this chapter are similar to those described in the 1973 NIOSH recommendations for TDI [37]. These control measures are frequently applicable in the control of polymeric diisocyanates as well.

The primary objective of engineering controls for operations using diisocyanates must be to reduce the concentrations of airborne diisocyanates so that they are at or below the recommended environmental limits. Process equipment should be designed so that the system is totally enclosed and operates, if possible, under negative gage pressure [9]. When it is necessary to open a vessel or when leaks or spills are likely, local exhaust ventilation systems should be provided. Unless other means can be used to control the concentrations of diisocyanates, the source should be fitted with a local exhaust ventilation system [9]. If a process is too large for this type of enclosure, dilution ventilation may be necessary.

Numerous polyurethane products exist, and the polyurethane may sometimes be formed under circumstances that are not readily adaptable to conventional exhaust ventilation procedures, eg, application of polyurethane foam to storage tanks to prevent corrosion. Some operations, such as spraying, mixing, foaming, injecting, flushing, pouring in place, and painting, can occur either in fixed locations or in the field. Workers engaged in these operations may require additional protection, such as positive pressure supplied-air respirators [37] and additional protective clothing. Although many types of diisocyanates are used in urethane foam systems, many of these systems contain polymeric isocyanates, which usually have lower vapor pressures [117]. For work with these polymeric isocyanates in field operations, where aerosols are likely to be generated, the same protection recommended for TDI should be used; the rate of dilution ventilation should be varied according to the rate of release of airborne particulate [117]. When planning exhaust ventilation systems to control diisocyanates, designers should consult Fundamentals Governing the Design and Operation of Local Exhaust Systems

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Z9.2-1971 [118] and Industrial Ventilation--Manual of Recommended Practice, the 1976 edition [119] or a later edition.

The concentration of diisocyanates in the workplace may also be decreased by substituting a compound with a lower vapor pressure. For example, where formulation considerations permit, MDI might be substituted for TDI [120]. In spraying and certain foaming operations where the diisocyanate is present in aerosol form, this substitution may not be an effective means of controlling exposure.

When ventilation requirements for any diisocyanate work area are determined, and it is established that an exhaust ventilation system is necessary, care must be taken in the placement of intake and exhaust vents [121]. Carroll et al [45] described respiratory sensitization from TDI in office workers as a result of TDI-contaminated air being drawn into the ventilation system of an office building from the exhaust vents of a neighboring factory using TDI. This report emphasizes the importance of determining that intake air for the ventilation system is not drawn from areas in which other diisocyanates are handled, and that exhaust vents be positioned to avoid exposure of other persons to the diisocyanate-contaminated air.

Sampling and Analysis

(a) Interfering Reactions With Airborne Chemicals

Because of the chemical reactivity of the diisocyanates, exposure to and measurement of diisocyanate monomers, as well as the effects of exposure to diisocyanates, may be complicated by reactions with other airborne chemicals. Dyson and Herman [122] examined the effect of relative humidity on TDI concentration as determined by the Marcali method [111]. This method measures TDI and one possible TDI hydrolysis product, toluene diamine, but not the TDI urea, 3,3'-diisocyanto-4,4'-dimethylcarbanilide. Humidified air was added in increasing amounts to dynamically produced, steady-state atmospheres of TDI (80% 2,4-TDI, 20% 2,6-TDI) initially determined to be at 34 or 400 ppb (240 or 2,800 μg/cu m). The relative humidity at 75 C achieved in the controlled reaction chamber by this procedure ranged from 0 to 80%. Increasing humidity was shown to cause linear decrease in the Marcali values, presumably reflecting increasing concentrations of TDI-urea. Regression analysis of the data determined that, independent of the TDI concentrations used, a decrease of 3.2% in the Marcali value would result with every increased unit of absolute humidity (in g water/kg dry air). The reaction of TDI with water was shown to be essentially complete within 75 seconds. For less chemically reactive diisocyanates such as HDI [123], hydrolysis would be expected to occur at considerably slower rates. The authors [122] concluded that increased humidity reduces the concentration of atmospheric TDI, but not to a degree that would prove useful as a routine control measure in the workplace. A decrease in apparent TDI concentrations due to humidity has also been observed by other investigators [44,111,124,125].

Volatilized amines may also be presented in workroom air where diisocyanates are being manufactured or used. Toluene diamine, a synthetic precursor to TDI and a possible hydrolysis product, is known to interfere positively in the Marcali determination of TDI [124,126,127]. Other primary aromatic amines would be expected to be positive interferences with any method in which diisocyanates are determined as secondary reaction products of their amine derivatives.

Meddle and Wood [126] developed a method for detecting aromatic isocyanates in air in the presence of primary aromatic amines. Individual air samples were bubbled through two different absorber solutions. A solution of dimethylformamide (DMF) and 1,6-diaminohexane (DH) was used to trap the primary aromatic amine and inactivate the isocyanate in one air sample. The second air sample was drawn through a solution of DMF, DH, and hydrochloric acid that traps the primary aromatic amine and hydrolyzes the isocyanate to its corresponding amine. The samples were then diazotized and coupled, and the amount of amine or isocyanate present was determined spectrophotometrically using standard calibration curves. The color in the DMF-DH absorbent solution is produced by the primary amine alone, and that in the DMF-DH-hydrochloric acid absorbent solution is produced by both the amine and the isocyanate. The amount of isocyanate present in the air sampled was determined by subtracting the former value from the latter.

Tertiary amines, such as triethylenediamine (TEDA), which are often used as catalysts in urethane polymerizations, have been shown to reduce the apparent concentration of airborne TDI [124,127]. Smith and Henderson [127] were the first to report the negative interference of TEDA vapors in the determination of gaseous TDI by the Marcali and Reilly tape methods. The fraction of apparent TDI loss, when analyzed by both methods, ranged from 49 to 88%. These results led the authors to question whether the tape and Marcali values were underestimating actual TDI exposure levels in polyurethane foaming operations. The reported degree of negative interference, however, appears independent of the TEDA concentrations. In addition, the ratios of TEDA to TDI examined, 17-262 [127], are 135-2,100 times those that might be expected during actual foaming or spraying operations [128,129].

In a later attempt to elucidate the mechanism of tertiary amine interference, Holland and Rooney [124] compared values obtained for TDI in mixed TDI-TEDA atmospheres by three analytical techniques: midget impinger sampling and analysis by the Marcali method, continuous-tape monotoring, and direct air-injection gas chromatography.

All methods gave similar values for TDI, and each showed similarly decreased values for the same TDI concentration in the presence of TEDA [124]. In contrast to the previous report [127], this study demonstrated that the reduction in measurable TDI exhibited some dependence on atmospheric amine concentration. A summary of the data shows that, at TEDA-to-TDI ratios of 9.6-25, about 90% of the input TDI could be measured; at a TEDA-to-TDI ratio of 105, only 21-25% could be measured. Six other catalysts used in polyurethane manufacturing were

said to give similar results. The effect of TEDA on measurable TDI was significantly reduced when glass components of the experimental apparatus were siliconized to decrease surface adsorption. The authors commented that gas chromatography did not detect any stable reaction intermediates, including toluene diamine, in the mixed gas stream. The only reaction product found proved to be the TDI urea that had formed as a white powder on the surface of the mixing system. The authors [127] concluded that all three analytical methods gave accurate measurements of atmospheric TDI in the presence or absence of tertiary amine catalysts and that the observed negative interference reflected an actual reduction in TDI concentration. Furthermore, the mechanism by which this reduction occurred may have depended on surface effects, relative humidity, and constituent concentration and residence time.

The above reports [124,127] suggest that the presence of tertiary amine vapors may catalyze the hydrolysis of airborne TDI to its urea. The reaction appears to be facilitated by absorption of one or more of the reactants to a surface [124]. Whereas gas chromatography of the mixed gases failed to isolate any stable reaction intermediate, the existence of short-lived, potentially toxic, reactive complexes in minute amounts cannot be discounted. Both studies [124,127] used concentrations of TDI that may be representative of actual working environments, 18-400 ppm; however, since the relative concentrations of amine used far exceeded realistic levels, the relevance of these results to the workplace situation remains questionable.

(b) Colorimetric Methods

Two methods, those of Marcali and Ranta, and modifications of them are most commonly used to measure aromatic isocyanate concentrations in air. The Marcali method [111] for measuring TDI involves bubbling the air sample through an acid absorber medium in which TDI is collected and hydrolyzed to the corresponding toluene diamine derivative. The amine is diazotized and coupled with 1-naphthyl ethylenediamine to produce a reddish-blue color. The intensity of this color is measured spectrophotometrically at 550 nm to provide an indication of the amount of TDI present. Marcali [111] reported that the method was capable of detecting 10 ppb (70 μg/cu m) of toluene-2,4-diisocyanate. He also determined that recovery of total TDI was apparently reduced when 35% toluene-2,6-diisocyanate was present. A similar reduction was reported by Meddle et al [44] for TDI mixtures containing 20 or 40% of the 2,6-isomer. To increase the accuracy of measuring mixtures of TDI isomers, both Marcali [111] and Meddle et al [44] recommended that standard curves be constructed with the appropriate isomer ratios. A portable field kit employing stable color standards could easily detect TDI at 50 ppb (360 μg/cu m) and could be modified to detect TDI at 20 ppb (140 μg/cu m). The method does not detect the TDI urea, 3,3'-diisocyanato-4,4'-dimethylcarbanilide, a hydrolysis product that is formed on reaction of TDI with water.

When Grim and Linch [94] examined the Marcali method for use with MDI, they found that 2 hours were required for complete color development. By

increasing the concentration of coupling reagent and partially neutralizing the absorber solution with sodium carbonate, the authors reduced the coupling time to 15 minutes. The 1974 NIOSH Manual of Recommended Analytical Methods [130] has incorporated the modifications of Grim and Linch [94] for routine measurement of MDI. The method as described can determine 7-73 ppb (70-750 µg/cu m) of MDI in 20 liters of air.

The Ranta method, as described by Zapp [36] and Marcali [111] can measure both TDI and TDI urea with equal efficiency and cannot distinguish between them. The compounds are collected by bubbling the air sample through a reagent solution of aqueous sodium nitrite, ethylene glycol monoethyl ether (Cellosolve), and boric acid. The intensity of the resulting orange-yellow color, measured at 450 nm, is proportional to the concentration of either compound.

On the basis of field and laboratory evaluations of these two methods, Skonieczny [131] concluded that the Marcali method was more suitable for field determination of peak concentrations and for detecting small amounts of TDI. Because the Ranta method requires a sampling time of 10-30 minutes to collect sufficient amounts of TDI under usual working conditions, Skonieczny noted that it might not detect momentarily high concentrations.

In the 1973 criteria document, NIOSH [37] recommended a method for sampling and analyzing TDI in air. Sampling was accomplished by drawing air through an all-glass midget impinger containing 15 ml of absorbing solution for 20 minutes at a rate of 2 liters/minute. For analysis, NIOSH recommended the Marcali method [111], incorporating modifications reported by Grim and Linch [94] and Larkin and Kupel [132]. Toluene diamine was used in place of TDI for standards, since it is less toxic and easier to work with at room temperature. The range of standards used was 1.0-20.0 µg of TDI or 3.5-70 ppb (25-500 µg/cu m) in a 40-liter air sample. The sensitivity of the method was said to be improved by increasing the length of the light path in the spectrophotometric cells. If amounts of TDI greater than 70 ppb must be measured, the final reagent solution can be diluted with absorber solution or a smaller air sample can be taken. Although MDI is detected by this method, the time required for complete color development under the prescribed conditions is 1-2 hours, compared with 5 minutes for TDI [94]. It is possible that TDI can be determined in the presence of MDI if the absorbance of the test solution is measured within 10 minutes after adding the coupling agent.

Various field test kits using the principles of the Marcali or Ranta method have been developed. These kits have simplified and standardized test procedures for on-site measurement. Grim and Linch [94] described a field kit for determining concentrations of TDI. Air was sampled through the standard midget impinger using a self-powered, constant-rate air aspirator. The sensitivity of the field kit employing the Marcali method was improved to allow detection of TDI at 10 ppb (70 µg/cu m) by collecting a larger volume of air and by reducing the volume of the reagent used. By increasing the coupling reagent concentration and adding sodium carbonate to the absorbing medium, the field kit could be used for

determinations of airborne MDI. The Ranta method was modified to allow measurement of TDI urea and TDI at concentrations as low as 10 ppb by increasing the volume of sample collected, reducing the volume of reagent used, and increasing the length of the light path in the colorimeter to 100 mm. To make the Ranta method suitable for field use, color standards that can be used with a portable visual comparator were developed and included in the kit.

Belisle [133,134] described a field kit suitable for measuring TDI in air. Air was sampled at a rate of 0.1 cu ft/minute through an acidified absorber solution in a modified midget impinger containing in situ-generated glutaconic aldehyde and cation-exchange resin. This process converts TDI to its corresponding amine, which reacts with glutaconic aldehyde to form an orange-red product. To measure the concentration of TDI, the orange-red color that appeared on the surface of the resin beads was matched against a set of color standards. Results reportedly agreed closely with those obtained by the Marcali method. A major advantage of this method is that the color develops while the air is being sampled. At a concentration of 10 ppb (70 µg/cu m) of TDI, sampling and analysis can be completed in 5 minutes. The method is capable of measuring TDI at 5 ppb (35 µg/cu m) in 0.5 cubic foot of air, and it may be modified to measure other aromatic isocyanates or aromatic amines by constructing appropriate calibration data.

Reilly [135] developed a field method for determining MDI in air. The sample was drawn through an acid absorber medium in which MDI was collected and hydrolyzed to the corresponding amine. The amine was diazotized and coupled with 3-hydroxy-2-naphthanilide to form a pinkish-orange azo compound. This was extracted into chloroform and compared visually with inorganic color standard solutions. The method was capable of measuring MDI at 10-40 ppb (100-400 µg/cu m) with a 5-liter sample of air. The equipment required is portable, and a complete determination can be accomplished in 12-15 minutes.

Meddle et al [44] extended the Grim and Linch adaptation [94] of the Marcali method to a general field-test procedure capable of detecting other aromatic diisocyanates in air. Procedures were described that established maximum sampling and analytical conditions for TDI, MDI, NDI, dianisidine disocyanate, and a polymeric form of MDI, polymethylene polyphenyl isocyanate. The authors noted that, with the exception of TDI, attempts to generate dynamic vapor atmospheres by bubbling dry nitrogen through liquified diisocyanates proved unsuccessful. Airborne concentrations produced by this method diminished rapidly indicating that these diisocyanates, where present in air, would be in aerosol form. Similar observations were made by Reilly [135] in his work with MDI. Analysis of all tested diisocyanates was subsequently performed on generated aerosol atmospheres [44]. A consequence of the aerosol nature of these test atmospheres was the adoption of a sintered dome bubbler for air sampling. To ensure complete recovery, aerosol particles trapped in the sintered dome during sampling were allowed time to dissolve in the absorber solution before coupling reagent was added. A 10-minute digestion time was judged sufficient under these conditions. Impinger

sampling at the same flowrate of 1 liter/minute was only 53% as efficient as sampling with the sintered dome bubbler. For use in the field, permanent color standards for MDI, NDI, TDI, and polymethylene polyphenyl isocyanate are available for concentrations of 10-40 ppb.

The aerosol nature of MDI in air was further supported by results of a recent study by Dharmarajan and Weill [116]. They found that MDI vapor generated by heating the diisocyanate to 110 C in a small enclosed room did not behave as a gas but rather as an aerosol. They compared the amount of MDI collected in absorbers according to the standard NIOSH-recommended method [130] with and without prefilters and found that 98% of the airborne MDI was collected on a Teflon filter backed with a cellulose pad and 87% was collected on the filter backed with a stainless-steel pad. Since the collection efficiency of the absorber for MDI aerosol was unknown in this study, it is likely that the actual amount of MDI in samples was higher than the amount detected. The percentage of the sample consisting of MDI aerosol could also have been underestimated. The authors also pointed out that since the major portion of MDI in air is present as an aerosol, concentrations of this compound should be reported in mg/cu m rather than ppm.

(c) Tape Methods

Reilly [136] developed a test-paper method to measure the concentration of TDI in air. A 5-liter air sample was drawn through a chemically treated filter paper at a rate of 1 liter/minute. After sampling was completed, stain was allowed to develop on the test paper for 15 minutes. The intensity of the stain was then compared with a set of color standards for TDI concentrations of 10, 20, 40, 60, and 100 ppb (70-700 μg/cu m). The method is specific for the aromatic diisocyanates, with no response obtained from the diamine derivatives. Several preparations of test paper, exposed to TDI at known concentrations, showed a variation in color development of about 20%. Qualitative tests indicate that the method may be adapted to detect MDI and NDI, and it is reported to require less analytical skill to perform than other methods.

Reilly's test-paper method was developed into a continuous monitor, the Dunlap/ICI Continuous TDI Monitor, which uses test-paper tape that moves continuously past a sampling port through which air is drawn by a vacuum pump. Fifteen minutes after it has been exposed to the air, the tape passes an optical readout head, and the intensity of the color produced by TDI on the tape is compared to an unexposed area of the tape and converted to concentrations. A strip-chart recorder connected to the instrument provides a permanent record of the measurements obtained. Miller and Mueller [137] evaluated the performance of this monitor by using the NIOSH-modified Marcali method [130] as a referent analytical procedure. When laboratory and field results were pooled and the data for the two methods compared by regression analysis, a correlation coefficient of 0.97 was found. It was suggested, however, that additional experimentation be done to determine the accuracy and precison of both methods for use in TDI

concentrations of 5 ppb (35 µg/cu m) or less. During the course of this study [137], the authors discovered that two midget impingers in series were necessary to trap airborne TDI adequately. Although the 1973 NIOSH criteria document [37] stated that a "single bubbler absorbs 95% of the diisocyanate if the concentration is below 2 ppm," Miller and Mueller determined that, at TDI concentrations ranging from 1 to 76 ppb (7-532 µg/cu m), the collection efficiency of the first bubbler was approximately 83%.

The Dunlap/ICI monitor has also been used to measure MDI under laboratory [116,138] and field [116,137] conditions. Development of tape color intensity in response to MDI, either as a vapor generated in toluene solution [138] or when spotted in known concentrations directly on the tape [116], was approximately 75% of the maximum when read at 15 minutes and the reaction was complete in 4 hours. Maximum color development with TDI, on the other hand, is complete at 15 minutes.

Where MDI may be found as a constituent of a reactive particulate, the accuracy of the monitor may be further reduced. In an initial test of the applicability of the Dunlap/ICI area monitor in MDI systems, results obtained by the monitor in foam and paint spraying operations were 36% and 35%, respectively [138], of those detected by the bubbler method of Meddle et al [44]. The author [138] explained that continued polymerization of MDI with other aerosol components would reduce the availability of reactive isocyanate functional groups for color formation.

Miller and Mueller [137] extended their evaluation of the TDI tape monitor for use in an MDI foaming operation. After applying the manufacturer's recommended correction factor, the authors found that the values obtained by the tape monitor at readings ranging from 1 to 5 ppb (10-50 µg/cu m) were in good agreement with those obtained by the spectrophotometric method.

Dharmarajan and Weill [116] assessed the performance of the TDI continuous tape monitor for analyzing both heat-generated and foam-spray-generated MDI aerosols. Eight-hour TWA concentrations of MDI in ppb determined by the monitors were compared with those obtained by the standard NIOSH-recommended method [130]. In the range of 5-8 ppb as determined by the NIOSH method, the tape monitors consistently gave readings indicating concentrations two to three times higher. The authors [116] explained this difference by pointing out that, whereas the filter tape medium of the monitors could be expected to collect 99.9% of the MDI aerosol, an impinger flowrate of 1 liter/minute would select against certain particle size populations. The absorber collection efficiency, however, was not determined in this study. Having emphasized the necessity for expressing MDI concentrations in units of mg/cu m, the authors devised a procedure for calibrating the TDI tape monitor for use in MDI aerosols. Known concentrations of MDI dissolved in toluene were spotted on the tape. After a time interval consistent with that used under workplace conditions, the tape was run through the photometric detector. Color intensity developed during this time could be

correlated with the known concentration of MDI in mg/cu m. However, the authors [116] did not test the validity of this calibration method in the workplace.

In view of these findings [116,138], it is important that calibration curves for continuous tape monitors used to detect MDI be constructed to simulate as closely as possible the actual conditions under which the monitor will be used.

The phenomenon described by a number of investigators [60,115,116,135,138], that MDI is rarely, if ever, found as a gas at ambient temperatures, has been shown to apply to NDI and dianisidine diisocyanate [44] and can be considered a general property of other diisocyanates that are solids or viscous liquids at room temperature.

(d) Chromatographic Methods

In 1974, Schanche and Hermann [125] described a paired sampling and analytical method that can reliably measure TDI concentrations in air in the ppb range. The sampling train consisted of three midget impingers connected in series, each containing 10 ml of chromatographic-grade toluene. To analyze TDI, the investigators used a gas chromatograph equipped with an electron-capture detector.

The impingers were connected by glass and Teflon connectors to prevent the surface absorption of TDI that would occur if synthetic or natural rubber connectors were used [125]. The sampling rate was limited to 1 liter/minute because at higher sampling rates the toluene in the impinger would bubble over into the next impinger in the series and because excessive evaporation of toluene could occur. The authors suggested that 0.1 ml should be the maximum allowable volume for evaporation for one impinger. This rate of evaporation would introduce an additional 1% error into the cumulative error for the resultant concentration. The total collection efficiency of this system was 98%, with the first impinger being 90% efficient.

The analytical system consisted of a Barber-Colman Series 5000 Selectra System gas chromatograph equipped with a tritium-source electron-capture detector [125]. A 4-foot Pyrex U-tube column (1/4-inch inner diameter) was packed with Chromosorb G (60/80 mesh) solid support coated with a mixture of Epon 1001 and Apiezon L. Oxygen-free nitrogen was used as the carrier gas at an optimum flowrate of 100 ml/minute at an inlet pressure of 15 psig. Operating temperatures were 150 C for the column and injection port and 170 C for the detector bath. The liquid sample size for injection was 5 μl [125]. Calibration curves were prepared by sequentially diluting TDI with chromatographic-grade toluene [125]. The calibration curves were then checked against a primary standard (TDI permeation tube). This paired system of sampling and analysis could accurately analyze TDI in a 10-liter sample of dry air at 1.4 ppb (10 μg/cu m). When the system was tested using air that had not been previously dried, readings were lower than expected. After appropriate corrections were made for the effects of humidity [122], the authors [125] obtained an overall efficiency of 97%.

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A thin-layer chromatographic (TLC) method was developed by Keller et al [113] for isolation and quantitative determination of various isocyanate compounds. The method is based on the reaction of isocyanates with N-4-nitrobenzyl-N-n-propylamine (nitro reagent) to form the corresponding ureas. The concentration of the ureas are then determined. The method is said to be capable of isolating and measuring diisocyanate monomers in the presence of partially polymerized reaction products. Concentrations of both monomer and free isocyanate-containing polymer can be determined.

Air in the working environment is sampled with two impingers containing a solution of the nitro reagent [113]. The solutions in the impingers are then combined and evaporated to dryness, and the remaining residue is dissolved in benzene. The benzene solution is chromatographically analyzed on thin-layer silica-gel plates, and ureas are visualized by reducing the nitro groups to amines and by diazotizing the amines with nitrous fumes. After evaporation of the nitrous fumes, the thin-layer chromatographic plates are sprayed with N-1-naphthyl ethylenediamine and quantitative determinations are made by visual comparison of the samples with standards. Scanning densitometry can be used for more accurate determinations. The lower limit for the determinations was found to be 80 µg/cu m for MDI, HDI, and TDI. The method, however, is time consuming and requires skilled attention to detail during the reduction and coupling steps.

A high-performance liquid chromatographic (HPLC) method for detecting isocyanates was developed by Dunlap et al [139]. Concentrations in work environments were determined by collecting the isocyanates with an impinger at a flowrate of 2 liters/minute into nitro reagent dissolved in toluene. The reaction product ureas were analyzed using HPLC with ultraviolet detection. Chromatographic separation of the ureas was accomplished on a pellicular silica HPLC column. As with the TLC method [113], both aliphatic and aromatic isocyanates can be analyzed. The HPLC method, however, extended the detection limits to 5, 5, and 10 µg of TDI, MDI, and HDI, respectively. The values were based on a 20-liter air sample and a 90-µl injection volume. The method cannot be used to analyze atmospheres that can oxidize or reduce the nitro reagent used in the impingers during sampling.

A similar but independently derived HPLC method has been described and extensively characterized by Vogt et al [123]. The study examined a variety of column matrices, sizes, packing protocols and solvent programs for the determination of nitro-urea derivatives of MDI, 2,4-TDI, 2,6-TDI, HDI, and a polymeric form (primarily trimer) of HDI, 1,3,5-tris-(6-isocyanatohexyl) biuret. Similar to the results of Dunlap et al [139], excellent resolution of mixed ureas was obtained. Depending on the experimental conditions [123], minimal detectable limits were slightly variable; 1.2-2.0 ng for MDI and 2,4-TDI, 1.2-5.0 ng for 2,6-TDI, 5.0-6.2 ng for HDI, and 40-240 ng for the HDI biuret. The apparent reaction times of the diisocyanates with nitro reagent, judged to be pertinent in field applications, were also measured. Maximum urea formation for MDI, 2,4-TDI, 2,6-TDI, and HDI was complete in 10, 10, 20, and 60 minutes, respectively.

Reproducibility was well within experimental error, relative standard deviations being generally below 15%. Urea derivatives for all tested isocyanates were reportedly stable for about 10 days.

A preliminary NIOSH study [140] of the HPLC analytical technique failed in its attempts to reproduce the results obtained by the developers of the method [32,123]. The report [140] cited the following reasons for failure: deterioration of silica gel columns caused by excess nitro reagent in samples; oxidation of the nitro reagent after sampling; shipping and exposure problems posed by the use of toluene in the collection medium. The time allotted for the study precluded an attempt to resolve these problems.

Two of these difficulties have already been addressed by previous investigators [123,139]. To eliminate excess nitro reagent in samples, Vogt et al [123] added p-tolyl isocyanate to the absorbing solution after the collected diisocyanates were allowed time (about 1 hour) to react. The resulting monourea derivative was observed to run well ahead of the diureas. Alternatively, column life was preserved from the effects of excess nitro reagent by daily flushing of the column with solvent.

Decomposition of nitro reagent during sampling in oxidizing or reducing atmospheres remains a serious disadvantage of this method [123,139]. The decomposition reported [140], however, appeared to be a result of insufficient purification of the synthesized nitro reagent and of the grade of toluene used. Nitro reagent is now commercially available. When the nitro reagent is dissolved in chromatographic-grade toluene, absorber solution impurities should be minimal. Compounds that will interefere with this procedure are those that absorb in the ultraviolet range and also have the same column retention time as the diisocyanate being investigated.

Toluene remains the solvent of choice for this method [123,139,140]. Federal regulations (49 CFR 172) allow air transportation of toluene in quantities of up to 1 quart/package. Where personal sampling procedures may expose workers to toluene vapor for extended periods, air sampler outlets could be fitted with an appropriate scrubber.

After reviewing the currently available analytical methods, NIOSH recommends the HPLC procedure described above [123,139]. This method is described in detail in Appendix I. Although the method may necessitate some initial experimentation before routine measurements can be made, it is the most sensitive method. Because quantities of diisocyanates in the nanogram range may be determined, relatively short sampling times are allowed. Analysis of the primary reaction product of diisocyanate and absorber ensures direct measurement of available isocyanate functional groups and precludes interference by other diisocyanate reaction products. The relative chemical stability of the nitro-ureas [123,139] allows for possible elapsed time between air sampling and subsequent analysis. In addition, the procedure is capable of separating and identifying mixtures of

diisocyanate monomers as well as mixtures of monomer and partially polymerized products [123,139]. The procedure has not been tested with diisocyanates other than TDI, MDI, and HDI. It is reasonable to assume, however, that a method which can effectively separate the isomers of TDI, as does the HPLC method, [123,139] can be used successfully for measuring other diisocyanates. Where possible interference from reducing or oxidizing atmospheres may be encountered, alternate sampling and analytical methods should be calibrated with the HPLC procedure.

Numerous studies have shown that absorber collection efficiency may vary dramatically [44,111,116,125,137]. It is therefore recommended that two serially connected impingers be used for air sampling until a reproducible collection efficiency is established for any given operation, after which a single impinger may be used for routine monitoring. The recommended flowrate of 2 liters/minute for 10 minutes represents a compromise for efficient aerosol and vapor sampling [115,116].