Selecting an Isocyanate Sampling and Analytical Method

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The ability to measure reactive isocyanate-containing compounds in air is important for assessing worker exposures in a variety of processes that produce or use surface coatings, polyurethane foams, adhesives, resins, elastomers, binders and sealants. Selecting the most appropriate sampling and analytical method for isocyanates in a specific workplace environment is difficult because isocyanates may be in the form of vapors or aerosols of various particle sizes; the species of interest are reactive and, therefore, unstable; pure analytical standards exist only for monomeric isocyanates; and low limits of detection are needed.

As a result, errors can be introduced during numerous points in the sampling and analytical procedures. If an inappropriate method is selected, the result can be either a gross underestimation of the exposure or a failure to detect airborne isocyanates. Therefore, the ability to select the best method is critical for an accurate assessment of the worker's isocyanate exposure.

Isocyanate Exposures

The feature common to all diisocyanates (monomers) is the presence of two -N=C=O (isocyanate) functional groups attached to an aromatic or aliphatic parent compound. Industry has made an important contribution to reducing isocyanate exposures by replacing low molecular weight isocyanate monomers with higher molecular weight isocyanate species that have similar characteristics, but are less volatile and therefore have a lower risk of inhalation exposure.

As a result, many prepolymer and polyisocyanate formulations commonly encountered in industry contain only a small fraction (usually less than 1 percent) of unreacted monomer. For example, the biuret of HDI consists of three molecules of HDI monomer joined together to form a higher molecular weight oligomer having similar characteristics to those found in the monomer. Also, many MDI product formulations consist of a combination of MDI monomer and oligomers (known as polymethylene polyphenyl isocyanate or polymeric MDI).

Not only are workers potentially exposed to a complex mixture of unreacted monomer, prepolymer, oligomer and/or polyisocyanate species found in a given product formulation, they can also be exposed to partially reacted isocyanate-containing intermediates formed during polyurethane production. In addition, isocyanate-containing mixtures of vapors and aerosols can be generated during the thermal degradation of polyurethane materials. Examples of such situations include welding of polyurethane-coated surfaces or breakdown of polyurethane binders present in foundry molds.

Exposure Standards

Exposure to isocyanates is irritating to the skin, mucous membranes, eyes and respiratory tract. The most common adverse health outcome associated with isocyanate exposure is asthma due to sensitization; less prevalent are contact dermatitis (both irritant and allergic forms) and hypersensitivity pneumonitis.

All isocyanate species formed during polyurethane production and thermal degradation, including monomers, prepolymers, oligomers and polyisocyanates, are capable of producing irritation to the skin, eyes, mucous membranes and respiratory tract. Respiratory sensitization has a 5 to 30 percent prevalence among workers in a variety of industrial processes. Experience has shown that both monomeric and polyisocyanate species are capable of producing respiratory sensitization in exposed workers. After sensitization, any exposure, even to levels below existing occupational exposure limits or standards, can produce an asthma-like response, which may be life-threatening.

Workplace inhalation exposure criteria have been established by a number of organizations. The primary sources of exposure criteria are the NIOSH Recommended Exposure Limits,[1] the ACGIH Threshold Limit Values® [2] and the OSHA Permissible Exposure Limits.[3] In addition, some states operating their

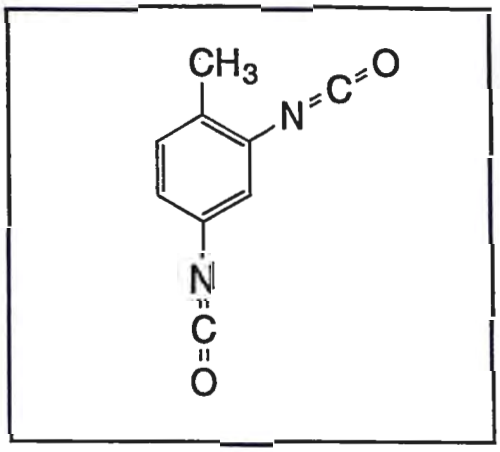

Figure 1. 2, 4,-TDI monomer.

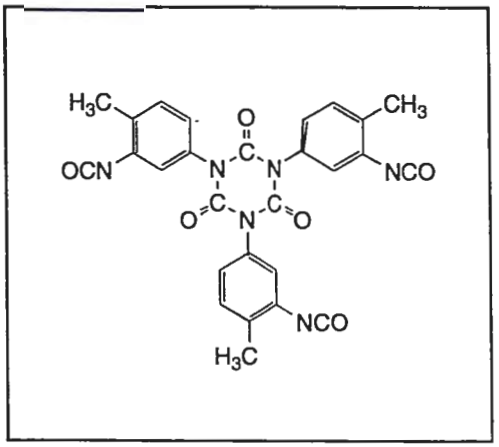

Figure 2. Polyisocyanate of TDI.

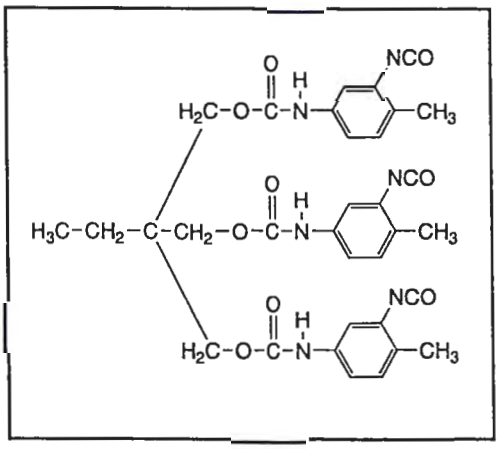

Figure 3. Prepolymer adduct of TDI and trimethylol propane.

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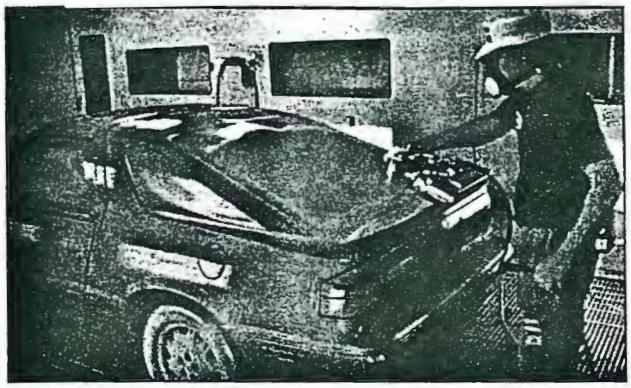

Figure 4. Auto body spray painting.

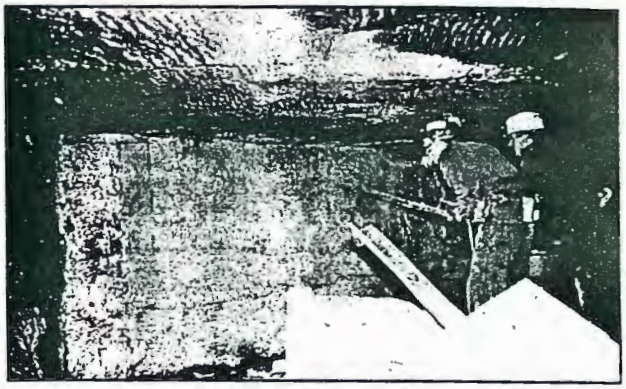

Figure 5. Mine shaft foam sealing.

own OSHA-approved job safety and health programs can have lower limits. These exposure criteria are for diisocyanate monomers.

Table 1 contains a comparison of the respective NIOSH RELs, ACGIH TLVs, OSHA PELs and United Kingdom Health and Safety Executive exposure criteria for the isocyanates. The UK-HSE has taken a different approach, i.e., developing a non-specific standard based on the total number of reactive isocyanate groups in a volume of air.[4] U.S. and U.K. isocyanate exposure standards are more similar than it may at first appear if molecular weights and number of isocyanate groups per molecule are taken into account. In general, six U.S. limits for isocyanate monomers and UK-HSE TRIG limits listed in Table 1 are based on an eight-hour time-weighted average exposure of approximately 5 parts per billion, or a short-term or ceiling exposure of approximately 20 ppb.

Both the U.S. and U.K. exposure standard approaches have limitations. The traditional substance-specific U.S. approach covers only a small number of monomeric diisocyanate species (currently TDI, MDI, HDI, HMDI, IPDI and NDI) and does not address the wide variety of isocyanate species and mixed isocyanate exposures now commonly encountered in the field. Conversely, the UK-HSE TRIG standard does not take into account that polyisocyanate species may be less toxic than monomeric species.

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Table 1—NIOSH, ACGIH, OSHA and UK-HSE Exposure Criteria for Isocyanates

Isocyanate Species	Exposure Criteria—Full-Shift TWAs Micrograms per cubic meter of air			Exposure Criteria—Short-Term or Ceiling Limits Micrograms per cubic meter of air			
	NIOSH REL	ACGIH TLV	UK-HSE	NIOSH REL Ceiling 10 min.	ACGIH TLV-STEL 15 min.	UK-HSE Ceiling	OSHA PEL Ceiling
TDI	CA-LFC	36	None	None	140	None	140
MDI	50	51	None	200	None	None	200
HDI	35	34	None	140	None	None	None
HMDI	None	54	None	210	None	None	None
IPDI	45	45	None	180	None	None	None
NDI	40	None	None	170	None	None	None
TRIG	None	None	20	None	None	70	None

Note: NIOSH considers TDI to be an occupational carcinogen (CA) and recommends that exposures be reduced to the lowest feasible concentration. TRIG = total reactive isocyanate group.

Table 2—Comparison of NIOSH and OSHA Isocyanate Methods

	NIOSH 5521	NIOSH 5522	NIOSH 2535	OSHA 42/47	PROPOSED NEW NIOSH[a]
Isocyanate a) Monomers	TDI, MDI, HDI, NDI, HMDI[b]	TDI, MDI, HDI, NDI, HMDI,[b] IPDI[b]	TDI, HDI	42 TDI, HDI 47 MDI	TDI, HDI, MDI, NDI,[b] HMDI,[b] IPDI[b]
b) Oligomers	HDI	TDI, MDI, HDI	None	None	HDI, MDI[b], TDI[b]
Sampler	Impinger	Impinger	Coated glass wool/opaque tube	Coated GFF	Impinger; GFF; impinger+GFF
Reagent	MOPP in toluene	Tryptamine in DMSO	Nitro reagent	1-2PP	MAP in butyl benzoate
Shelf Life	7d 0°C	6 mo 25° C in dark	7d 25°C in dark	42 0.1 mg; 47 1 mg 6 mo 0°C sealed	Unknown
Sampling Rate Volume	1 L/min 5-500 L	1-2 L/min 15-360 L	0.2-1 L/min 2-170 L	1 L/min 15 L	1-2 L/min 1-500 L
Personal	No	No	Yes	Yes	Yes
Vapor	Yes	Yes	Yes	Yes	Yes
Particles ≤ 2 µm	No	No	No	Yes	Impinger: No Filter: Yes
Particles ≥ 2 µm a) Half-life of product > 3x sampling time	Yes	Yes	No	No[c]	Impinger: Yes Filter: Yes (with immediate field extraction)
b) Half-life of product < 3x sampling time	Yes	Yes	No	No	Impinger: Yes Filter: No
Sample Stability	7d 25°C: 78% 7d 4°C: 88%	28d 25°C in dark: 95-104%	14d 25°C: 91%	15d 22°C: 42 80-86%; 47 94.8%	Unknown
Laboratory Sample Preparation	Impinger: evap/ redissolve in methanol	None	Ultrasonic extraction in methanol	Extraction in ACN/DMSO, 9 /1	Impinger: SPE Filter: extract or SPE
Technique	HPLC/RP, isocratic	HPLC/RP, isocratic/gradient	HPLC RP, isocratic	HPLC/RP, isocratic	HPLC/RP, gradient
Detector 1 LOD[d]: a) Amount injected b) 15 L air conc.	UV @ 242 nm/PDA 14 pmol 1.2 ppb	FL ex 275 nm em 320 nm 0.7 pmol 0.9 ppb	UV @ 254 nm 14 pmol 0.9 ppb	FL ex 240 nm em 370 nm 47 0.2 pmol 47 0.06 ppb	UV @ 253 nm 0.5 pmol 0.08 ppb
Detector 2 LOD[d]: a) Amount injected b) 15 L air conc	EC (+ 0.8V) 0.5 pmol 0.04 ppb	EC (+ 0.8V) 4.4 pmol 5.7 ppb	None	UV @ 254 nm 42 1.0-1.1 pmol 42 0.13-0.14 ppb	FL ex 250 nm em 409 nm est. ~ 5 fmol est. ~ 0.8 ppt
Identification	Monomer: Retention Time Aliphatic oligomers: PDA	Monomer: FL Retention Time Other isocyanate: EC confirmation	Retention Time	Retention Time	Monomer: Retention Time Other isocyanate: UV/FL ratio

a This method is under development; procedures may change somewhat pending validation.
b Determination possible; lacks validation data.
c Usually underestimates concentration; immediate field extraction may improve accuracy.
d Instrumental limit of detection.

Abbreviations: ACN = acetonitrile; conc = concentration; d = days; DMSO = dimethyl sulfoxide; EC = electrochemical detector; em = emission; evap = evaporate; ex = excitation; FL = fluorescence detector; GFF = glass fiber filter; HPLC = high-performance liquid chromatography; LOD = limit of detection; MAP = 1-(9-anthracenylmethyl)piperazine; mo = months; MOPP = 1-(2-methoxyphenyl)piperazine; nitro reagent = N-[(4-nitrophenyl) methyl] propylamine; PDA = photodiode array detector; 1-2PP = 1-(2-pyridyl)piperazine; RP = reversed phase; SPE = solid phase extraction; UV = ultraviolet detector.

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A more complete discussion of isocyanate health effects with associated references and isocyanate exposure standards is presented in a chapter on the determination of airborne isocyanate exposures contained in the *NIOSH Manual of Analytical Methods*[5] and in a similar *AIHAJ* article.[6]

Sampling and Analytical Method Selection

The capability to measure all isocyanate-containing substances in air, whether they are in monomer, prepolymer, oligomer and polyisocyanate forms found in the original formulation or intermediate forms produced during the industrial process, is important when assessing a worker's total airborne isocyanate exposure. All published sampling and analytical methods have significant limitations.

Table 2 summarizes OSHA and NIOSH isocyanate methods and gives the criteria for choosing a method. Selection depends on the chemical nature of the isocyanate species, the physical state of the isocyanate species, the cure rate of the product, the required sampling time, whether personal or area sampling is required and the sensitivity of detection needed, as shown in Table 2. Measurement accuracy, selectivity and sensitivity are considered for the entire sampling and analytical measurement process including collection, derivatization, sample preparation, separation, identification and quantification.

Unfortunately, the need to measure highly reactive isocyanate species at low levels is many times in conflict with the desire of industrial hygienists and chemists to choose methods that are convenient to use in the field and easy to run in the laboratory. It is also in conflict with the desire of employers to select the least expensive method for monitoring or to conduct monitoring limited to demonstrating compliance with existing U.S. regulatory exposure standards.

This information is used to select methods for NIOSH research studies and health hazard evaluations. It is provided when employers, industrial hygienists or laboratories request NIOSH technical assistance on isocyanate methods. A thorough discussion of the sampling and analytical issues and the advantages and disadvantages of isocyanate sampling and analytical methods used in the United States and abroad is contained both in the *NMAM®* and in an updated *AIHAJ* article on the subject.[5,6]

All isocyanate sampling and analytical methods have significant limitations that affect the ability of organizations to ensure that exposures are minimized and controlled. These limitations also affect the ability of regulatory and voluntary standard-setting organizations to set exposure standards. More research is needed to resolve the limitations of current sampling and analytical methods. Such research is ongoing at NIOSH and elsewhere in government, academia and the private sector. Therefore, this guidance is subject to revision as isocyanate exposure standards change and as new or improved isocyanate measurement methods are developed and published.

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