Occupational Hygiene Air Monitoring for MDI & TDI Guidance

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Purpose

This guidance document has been prepared by the American Chemistry Council (ACC) Center for the Polyurethanes Industry (CPI) to describe workplace air monitoring methods for methylenediphenyl diisocyanate (MDI) and toluene diisocyanate (TDI), and to provide information on personal and area sample collection. Several instruments and derivatization methods for monitoring vapors are presented.

Overview

Diisocyanates are reactive compounds, and therefore, evaluating airborne concentrations of MDI and TDI can be very challenging. Diisocyanates react with amines, alcohols, hydroxides and even water to form various compounds. Therefore, to assess real-time airborne concentrations of MDI or TDI, both direct and indirect air sampling methods typically involve the use of a paper tape or filter coated with a reagent that reacts with diisocyanates to form a stable derivative.

The most common direct read instruments used are based on treated paper tape technology. The instrument draws air through a reagent-coated paper tape and senses the degree of color change on the tape which results from formation of the colored derivative upon reaction with a diisocyanate and reports the airborne concentration of MDI or TDI in parts per billion (ppb). Indirect sampling methods typically use an amine treated filter or solution which converts the diisocyanate to a stable urea derivative for laboratory analysis. It is common for analytical laboratories to report the MDI or TDI results in either micrograms per cubic meter (µg/m3) or ppb. There are other direct read instruments and indirect sampling methods/ technologies available for both MDI and TDI. These will be briefly discussed later in this document.

Another easy-to-use direct read device for measuring airborne concentrations of MDI or TDI vapors is a passive diffusion

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badge. Passive badges use the same principle as paper tape direct read instruments except that they rely on passive diffusion of the diisocyanate in the air for sampling and the color change is read visually instead of by a photometric instrument. The passive badge has a specific spot where a color change appears (i.e., pink/red color) if MDI or TDI is present. Upon completion of the monitoring period, a color comparator wheel is used to determine the airborne concentration in ppb.

It is generally accepted that indirect sampling methods (i.e., treated filter or impinger solution sent to a lab for analysis) provide more accurate quantitation and greater sensitivity (e.g., can report lower airborne concentrations) than direct read instruments for most PU applications. Exceptions may include where one has confirmed that the application or process being evaluated produces only MDI or TDI vapors and that there are no other gases/vapors (i.e., carbon monoxide, nitrogen oxides) present that could cause an interference with the instrument.

Indirect methods for collecting personal air samples involve attaching the sampling device (i.e., treated filter or impinger) in the employee's breathing zone (e.g., clipped to the workers shirt collar or near the shoulder area). This requires the worker to wear a small air sampling pump that must be calibrated prior to and following the sampling period so that the laboratory knows the air sample volume (e.g., cubic meters of air sampled). Personal air samples may be collected over a period of hours or over a shorter time period (15-minutes) if the worker performs a specific task or job function that is of short duration.

Area air samples collected at key locations along a production line or in adjacent work areas help to further characterize airborne MDI or TDI concentrations. The area sample results can be used to assess the risk of exposure in specific work locations or to identify areas that require special attention. Area sample results also may be used to evaluate how well a ventilation system is operating and for determining where respiratory protection is needed.

To choose the proper air sampling approach for MDI or TDI, it is very important to know the physical state (e.g., vapor, mist, coated solid particle, or condensation aerosol) of the diisocyanate that may be released into the air from the specific polyurethane application being evaluated. This can sometimes be difficult to determine for processes/applications involving the use of MDI or polymeric MDI because of the very low volatility of this chemical. MDI can exist in air as a vapor, condensation aerosol, or can be adsorbed on the surface of a solid particle in air such as a wood fiber or dust particle. Many direct read instruments/badges will not accurately read concentrations for applications/processes that produce an aerosol; it is important to understand the limitations that exist when determining which sampling method to use.

There are published occupational exposure limits (OELs) in the United States for MDI and TDI. OELs are published by the Occupational Safety and Health Administration (OSHA), the American Conference of Governmental Industrial Hygienists (ACGIH) and

the National Institute for Occupational Safety and Health (NIOSH). Most exposure limits for MDI and TDI are based only on the monomeric concentration of MDI and TDI.

In the US, OSHA-permissible exposure limits (PELs), ACGIH Threshold Limit Values (TLVs), and NIOSH Recommended Exposure Limits (RELs) for many chemicals are expressed as an 8-hour time-weighted average (8-hr TWA), or a short-term exposure limit (STEL) based on 15 minutes, or a ceiling (C) limit not to exceed for any length of time. These values are commonly found on manufacturer Safety Data Sheets (SDSs).

Note: The following is not a definitive list of available instruments or methods. Inclusion in this listing is not intended to be an endorsement of any particular method by CPI or its members, and not a warranty of the effectiveness or fitness for a particular purpose of any listed device or method.

Examples of Direct Reading Instruments or Devices

These instruments are generally used for monitoring vapors rather than particulates. Consider the type of application and any limitations of the device and consult with the device manufacture or chemical manufacturer. In general, detector tubes, badges, and colorimetric paper tape instruments are direct reading instruments or devices that can be used for measuring diisocyanates. Examples of these instruments are described below.

Colorimetric Detector Tubes

Below are examples of detector tubes that may be used for sampling of MDI and TDI.

TDI Dräger Tube 0.02/A (Dräger)

This tube requires sampling pump – colorimetric reaction with TDI – discoloration compared to color comparison tube

(measurement range ~ 0.02-0.2 ppm)

IsoSense Sampling Kit for MDI or TDI (DOD Technologies Inc.)

- Sampling unit (Pump) with belt clip
- 20 test strips (Isocyanates)
- Battery Charger
- Concentration Calculator
- Sampling Holder & tubing
- Manual
- Flow test kit
- Carrying Case

(measurement range - down to ~1ppb)

Passive Badges

Below are examples of passive badges that may be used for sampling of MDI and TDI.

MDI and TDI passive sampler (MORPHIX SafeAir®)

Colorimetric badge – diffusion-based passive sampling; color reaction (of the badge) with isocyanate. Quantification is measured using a color comparator.

(measurement range – 2.5 to 200 ppb-hr for MDI & 2.5 to 700 ppb/hr for TDI)

TDI Dosimeter Badge (DOD Technologies Inc.)

(TDI only - 10 PPB/hours (min) & 385 PPB/hours (max))

CHEMTEQ Aromatic Diisocyanates Area Monitor (CHEMTEQ)

(minimum detectable limit: 4ppb•hr; service time: 20 h)

Colorimetric Paper Tape Instruments

Generally, area (stationary) monitoring devices generate short period and/or time weighted average (TWA) values. They have the capability of data logging and can be used for MDI, TDI and other diisocyanates such as hexamethylene diisocyanate (HDI).

Paper tapes have a limited shelf life. Use in accordance with the manufacturer's instructions.

ChemKey™ TLD Toxic Gas Detector

(measurement range ~2 to 60 ppb)

SPM Single Point Monitor

(measurement range – most diisocyanates (including HDI,MDI & TDI) ~ 2 to 60 ppb)

ChemLogic 1

Single Point Continuous Monitor

(measurement range 0 to 100 ppb & 0 to 200 ppb MDI & TDI)

CLPX

(measurement range ~0 to 200 ppb MDI & TDI; ~0 to 200 ppb)

Paper tape instruments illustrated below are no longer commercially available but may still be in use:

GMD AutoStep Plus®

(measurement range ~1 to 200 ppb MDI & TDI; ~1 to 500 ppb HDI)

NextStep®

(measurement range ~0 to 200 ppb MDI & TDI; ~0 to 200 ppb HDI)

GMD Remote Intelligent Sensor (RIS)

(measurement range ~1 to 2000 ppb for TDI; ~1 to 200ppb for MDI)

Ion Mobility Spectrometer

Ion-mobility spectrometry (IMS) is an analytical technique used to separate and identify ionized molecules in the gas phase based on their mobility in a carrier buffer gas. Portable and fixed IMS monitors are available by various vendors.

RAID-M100Plus

(measurement range ~0 to 50 ppb TDI)

Examples of Equipment Used for Indirect Sampling Methods

As previously stated, indirect sampling methods utilize air sampling pumps to draw air through treated filters and/or impingers, followed by laboratory analysis of the sampling media. Note that treated filters can be desorbed in the field. The photographs below illustrate some of the equipment that is used.

Air sampling pump with open-face treated 37mm filter.

Treated 37mm filters in plastic cassettes.

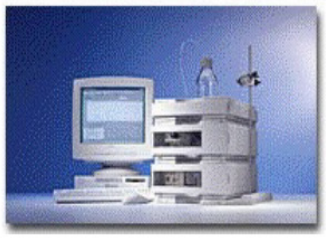
Air sampling pump with impinger and back-up treated 13mm filter.

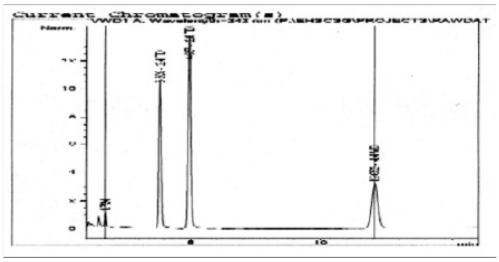
Glass impingers.

Asset EZ4®-NCO Dry Sampler.

Treated 13mm filters in plastic cassettes (e.g., Swinnex).

Note that indirect methods require standards and analytical facilities.





High Performance Liquid Chromatography (HPLC) Instrument (left) and Chromatogram (right).

Published Air Sampling & Analytical Methods

ISO 17734-1:2006 - Impinger/filter or tube/filter containing, impregnated or coated with DBA

ISO 16702:2007 - 1,2MP coated GFF and/or impinge (UK MDHS 25/3) (suitable for total isocyanates)

ISO 17735:2019 - MAP coated GFF and/or impinger (suitable for total isocyanates)

ISO 17736:2010 - 1,2MP – MAMA double-coated filter sampling (short-term sampling only)

NIOSH 5521 - Impinger -1,2MP toluene (suitable for total isocyanates)

NIOSH 5522 - Impinger (tryptamine in DMSO)

NIOSH 2535 - Tube containing nitro reagent coated glass wool

OSHA 5002 1,2PP coated GFF (former OSHA Methods 42 and 47 are superseded by OSHA 5002)

Abbreviations

1,2MP	1-(2-methoxyphenyl)piperazine
1-2PP	1-(2-pyridyl)piperazine
DBA	dibutylamine
DMSO	dimethyl sulphoxide
GFF	glass fibre filter
HDI	hexamethylene diisocyanate
HPLC	high performance liquid chromatography
MDI	methylenediphenyl diisocyanate
MAMA	9-(methylaminomethyl)-anthracene
MAP	1-(9-anthracenylmethyl)piperazine
Nitro reagent	N-[(4-nitrophenyl) methyl] propylamine
TDI	toluene diisocyanate
TWA	time weighted average

Useful Documents

Guidelines for selecting analytical methods for sampling and analyzing isocyanates in air.

ISO/TR 17737:2007

Determination of Airborne Isocyanate Exposure.

http://www.cdc.gov/niosh/docs/2003-154/pdfs/chapter-k.pdf

Considerations for Modifications to OSHA Method 42 Air Monitoring Method: Toluene Diisocyanate (TDI) (americanchemistry.com)

Considerations for Modifications to OSHA Method 47 Air Monitoring Method: Diphenylmethane Diisocyanate (MDI) (americanchemistry.com)

Useful Websites

Examples of Instruments and Equipment	
Dräger	http://www.draeger.com
MORPHIX (K&M Environmental)	https://www.morphtec.com/
Honeywell Analytics (MDA)	http://www.honeywellanalytics.com
DOD Technologies Inc.	http://www.dodtec.com/
Bruker Daltonics	https://www.bruker.com/
Sampling pumps & equipment– Casella	https://www.casellasolutions.com/
Gasmet Technologies	https://www.gasmet.com/
SKC	http://www.skc.com/

Examples of Methods	
HSE Publications	http://www.hse.gov.uk/pubns/mdhs/index.htm
NIOSH	http://www.cdc.gov/niosh/topics/isocyanates/
OSHA	http://www.osha.gov/
UK HSE	http://www.hse.gov.uk/
ISO	https://www.iso.org/home

Analytical Reagents and Standards	
Sigma - Aldrich	http://www.sigmaaldrich.com/

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American Chemistry Council
700 2nd Street, NE
Washington, DC 20002
(202) 249-7000
www.americanchemistry.com