



# Calibration of a Direct Reading Airborne MDI Monitor for Monitoring HDI Biuret and HDI Isocyanurate Aerosols

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## HDI Prepolymers

Prepolymers of Hexamethyl Diisocyanate (HDI) are being used extensively in polyurethane formulations.

- The Biuret of HDI is made through the condensation of 3 HDI molecules with 1 water molecule
- The Isocyanurate of HDI is a trimer of HDI formed through self condensation

## Properties of HDI Prepolymers

- Less volatile than monomeric HDI
- Less reactive with atmospheric moisture than monomeric HDI
- These properties make HDI Biuret and Isocyanurate well suited to paint and coating applications

## Exposure to HDI Prepolymers

- Health effects include occupational asthma and sensitization
- Major exposure route is inhalation of aerosol and vapor during application
- Affected industries
  - Automobile manufacturing and repair
  - Architectural painting and refinishing
  - Wood finishing operations

## Airborne Exposure Guidelines for HDI Prepolymers

- No ACGIH TLV available
- No OSHA PEL available
- Oregon State recommended exposure limit
  - 0.5 mg/m<sup>3</sup> 8 hour TWA, 1.0 mg/m<sup>3</sup> STEL
- Bayer Corporation guideline (1) limit
  - 0.5 mg/m<sup>3</sup> 8 hour TWA, 1.0 mg/m<sup>3</sup> STEL

## Airborne Monitoring Methods for HDI Prepolymers

- Liquid impinger methods
  - Example: Nitro-Reagent - HPLC

- Filter Collection

- Example: Iso-Check Filter System - HPLC

- There is no currently available direct reading instrument for the measurement of workplace concentrations of HDI prepolymers

### Advantages of Direct Reading Instruments (DRI)

- DRI provide measurements of the actual workplace airborne concentrations in real time or near real time
- DRI can therefore alert workers to sudden changes in concentrations
  - Emergency response situations
  - Location of emission sources
  - Monitoring the progress of clean up efforts

### Goal of this Study

- To determine if any correlation exists between the response of a commercial MDI DRI and the concentration of HDI Biuret and HDI Isocyanurate under laboratory conditions
  - This is a necessary first step in determining whether this DRI can be used in field situations

### MDI Monitor Used in the Tests

- GMD Systems RIS Model 720-120
- Previous testing showed good performance in tests with airborne MDI aerosols
- Employs detection chemistry which is specific to the isocyanate group and not to specific isocyanate compounds

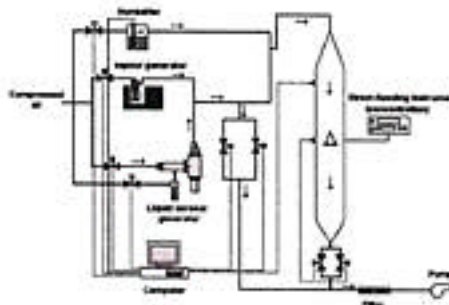
### Method Used to Verify the Challenge Concentrations

- Sampling of atmospheres using Iso-Check System
- Allows simultaneous determination of both the HDI monomer and prepolymer concentrations
- Requires HPLC quantitation

### Experimental Protocol

- Set generation conditions for desired aerosol concentration level and allow to equilibrate
- Allow the DRI to sample the generated aerosol for at least 45 minutes and record readings
- The DRI reading is taken to be the average over the exposure period
- At the same time, actual monomer and prepolymer concentrations are determined by the reference method
- All tests run at room temperature and 50% relative humidity

### Chamber Diagram



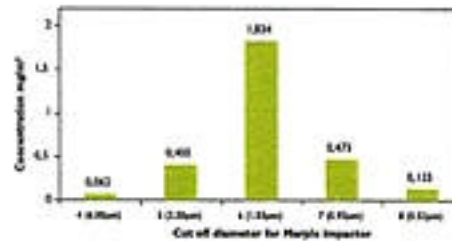
## Aerosol Generation

- Products Tested:

- HDI Biuret - Desmodur N 3300 (Bayer)
- HDI Isocyanurate - Desmodur N 3300 (Bayer)

- The ratio of monomer to prepolymer in the generated aerosol was consistent with the ratio reported in field studies(2)
- Generated aerosol was the same for each product

## Particle Size Distribution



## Data Treatment

- Referee method gives both the monomer and prepolymer concentrations at the time of the DRI test
- These are used to determine an equivalent HDI concentration for the test
- Linear regression used to determine the correlation between the average DRI reading and the chamber concentration

## Conclusions

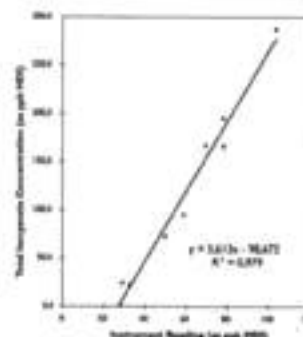
- Correlation exists between the MDI monitor response and the total airborne concentration of HDI Biuret and HDI Isocyanurate
- The data showed the ability of the MDI monitor to effectively sample isocyanate aerosols
- For HDI Biuret:
  - Correlation coefficient was 0.979
  - Correlated over a wide range of monomer to oligomer ratios

## For HDI Isocyanurate:

- Correlation coefficient was 0.9575
- Correlation was tested at low monomer to oligomer ratios

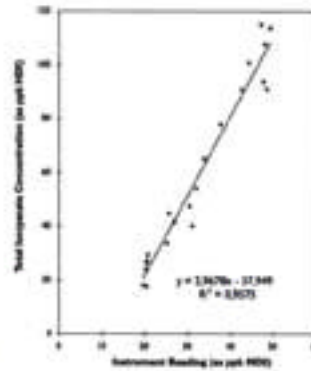
## Data Table and Graph for HDI Biuret (Desmodur N 3200)

HDI Monomer Conc. (mg/m³)	Biuret Oligomer Conc. (mg/m³)	Monomer/Oligomer Ratio	Total Conc. as µg/m HDI	Average DRI Reading (µg/m HDI)
0.008	0.000	—	1.1	28.2
0.008	0.145	0.055	21.9	33.0
0.004	0.145	0.034	24.4	29.2
0.181	0.228	0.082	72.7	50.3
0.180	0.478	0.376	94.9	59.7
0.120	1.040	0.113	142.7	78.4
0.264	1.180	0.058	146.3	89.8
0.264	1.287	0.051	194.7	78.5
0.120	1.866	0.064	206.6	103.9



## Data Table and Graph for HDI Isocyanurate (Desmodur N 3300)

HDI Monomer Conc. (mg/hr)	Isocyanates Oligomer Conc. (mg/hr)	Monomer/ Oligomer Ratio	Total Conc. as ppb HDI	Average DRG Reading (ppb HDI)
0.011	0.412	0.028	90.4	43.6
0.011	0.033	0.021	77.4	37.7
0.019	0.408	0.023	45.1	33.8
0.004	0.237	0.018	33.4	33.3
0.003	0.282	0.011	41.3	34.9
0.004	0.304	0.013	44.8	35.7
0.003	0.160	0.019	33.8	30.2
0.002	0.119	0.017	17.3	30.4
0.002	0.122	0.016	18.0	19.7
0.001	0.044	0.002	93.8	47.7
0.007	0.017	0.011	90.8	46.4
0.007	0.704	0.010	107.7	48.1
0.002	0.185	0.011	37.1	30.5
0.002	0.176	0.011	36.1	30.4
0.002	0.190	0.010	38.1	30.7
0.002	0.223	0.009	47.4	30.5
0.005	0.247	0.014	54.0	31.1
0.003	0.275	0.011	40.1	31.0
0.007	0.704	0.009	113.8	49.3
0.008	0.703	0.010	114.9	47.2
0.005	0.688	0.007	100.7	44.3



## References

1. Bayer, Inc.: Hexamethyl Diisocyanate Based Polyisocyanates, Health and Safety Information, Pittsburgh, PA: 1992
2. LESAGE J., GOYER N., DESJARDINS F., VINCENT J-Y., PERRAULT G., "Workers' Exposure to Isocyanates". Am. Ind. Hyg. Assoc. J., Vol 53, no 2, p. 146-153 (1992).